CArbon-14 Source Term

CAST

Advisory Group Review of Year 1 WP Annual Reports and Minutes of Second CAST GAM (D1.5)

Compiled E. Scourse

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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.

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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Executive Summary

The CAST Project has initiated a 'CAST Advisory Group' made up of two independent experts and representatives from the CAST End-Users 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 final deliverables from each of the Work Packages for the CAST project prior to publication on the CAST website. The independent experts are:

- Dr. Fraser King, Integrity Corrosion Consulting Limited, and

- Dr. Irka Hajdas, an independent consultant.

In addition to the two independent experts, the CAST project engages with numerous end-users of the outputs from the research, via an 'End-Users Group'. The members of the End-Users Group include representatives from: Ondraf/Niras, RWM, Nagra, GRS, LEI, Surao, SKB and Andra. A high-level review was undertaken by these representatives of the WP Annual Reports.

The reports reviewed by the CAST Advisory Group for this report are:

- D1.4 CAST General Assembly Meeting and Minutes - Year 2;

- D2.2 WP2 Steels Annual Report – Year 1;
- D3.5 WP3 Zircaloy Annual Report – Year 1;
- D4.2 WP4 Ion-Exchange Resins Annual Report – Year 1;
- D5.2 WP5 Graphite Annual Report – Year 1.

This report collates the comments from the CAST Advisory Group into the following sections:

- Section 2 – Review by Dr. Fraser King;
- Section 3 – Review by Dr. Irka Hajdas;
- Section 4 – End-User reviews

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1 Introduction

1.1 *CAST Advisory Group*

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. The independent experts are:

- Dr Fraser King. Fraser has 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. Irka 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.

1.2 *CAST End-User Group*

In addition to the two independent experts, the CAST project engages with numerous end-users of the outputs from the research, via an ‘End-Users Group’. The members of the End-Users Group include representatives from Ondraf/Niras, RWM, Nagra, GRS, LEI, Surao, SKB and Andra. The main objective of the End-Users Group is to ensure that the outputs from CAST meet the needs of the Waste Management Organisations and are relevant to the development of safety cases and safety assessments in the national programmes. A high-level review was undertaken by these representatives of the WP Annual Reports. This review aims to help steer the research projects within CAST to ensure that the outputs are suitable and meeting the requirements of the end-users of the information; and to determine if the output from the research projects is meeting the requirements for the end-users and can be used in the safety assessments in their national programmes. The comments from the End-Users are collated in ‘Section 3 – End-Users Review’.

1.3 *Review Structure*

The reports reviewed by the CAST Advisory Group for this report are:

- D1.4 CAST General Assembly Meeting and Minutes - Year 2 (Scourse and Williams, 2014);
- D2.2 WP2 Steels Annual Report – Year 1 (Mibus et al, 2015);
- D3.5 WP3 Zircaloy Annual Report – Year 1 (Necib et al, 2014);
- D4.2 WP4 Ion-Exchange Resins Annual Report – Year 1 (Reiller et al, 2014);
- D5.2 WP5 Graphite Annual Report – Year 1 (Norris et al, 2015).

This report collates the comments from the CAST Advisory Group into the following sections:

- Section 2 – Reviews by Dr. Fraser King;
- Section 3 – Reviews by Dr. Irka Hajdas;
- Section 4 – End-User reviews

2 Review of 2014 GAM Minutes and Year 1 Work Package Annual Reports by Dr. Fraser King

2.1 *Introduction*

One of the tasks of the CAST Advisory Group is to review progress towards meeting the various project goals. The progress towards meeting the overall aims of the CAST project is judged against the framework of a ^{14}C source-term described by King and Hajdas (2015). Briefly, that framework describes the required knowledge in three key areas, namely:

- Inventory (the quantity, chemical nature, and physical distribution of ^{14}C in the waste form);
- Release (the rate and mechanism of release of ^{14}C from the waste form to the immediate environment);
- Transport/reaction (the transport and possible subsequent reactions of ^{14}C in the near- and far-field environments).

This overall framework is schematically illustrated in Figure 1 for the case of oxide-covered metallic waste forms.

The required data and mechanistic understanding could come from existing information in the literature or from new information produced within the CAST project.

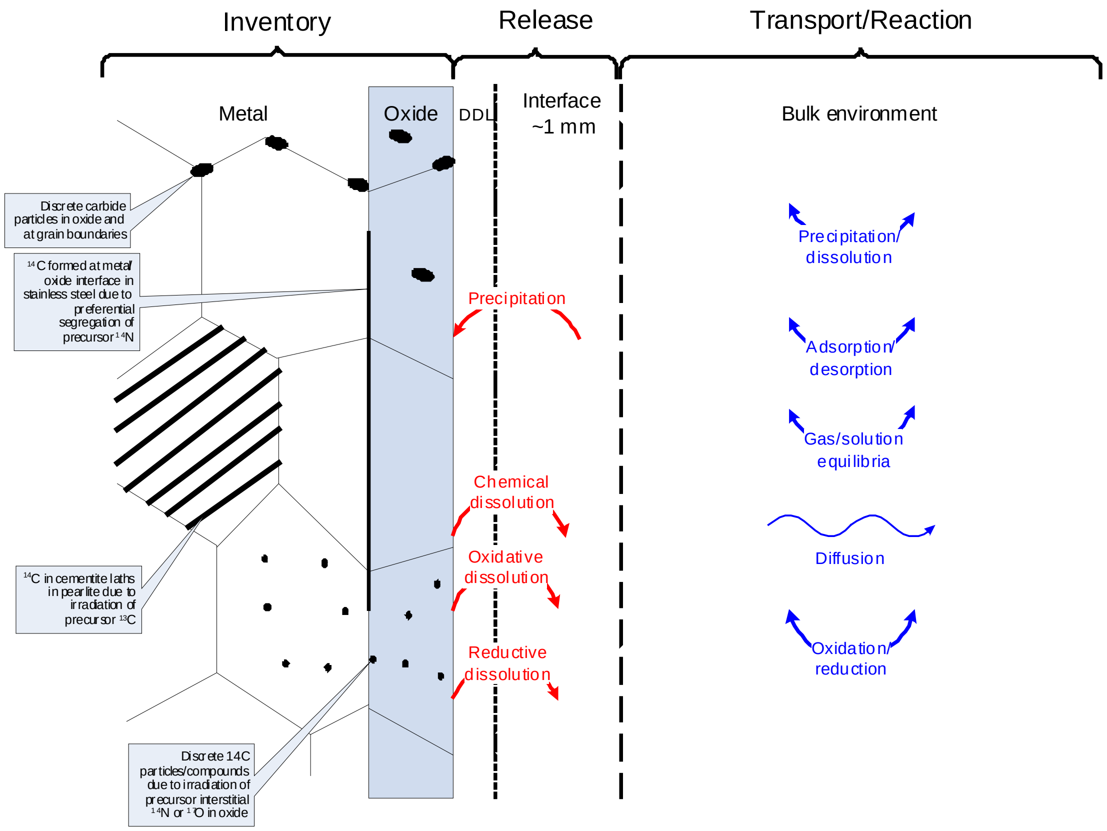

Figure 1: Schematic Illustration of Processes and Features of Possible Importance in the Development of a Source-term Model for the Release of ^{14}C from Irradiated Metals.

2.2 D1.4 Minutes of CAST General Assembly Meeting 2

The second CAST General Assembly Meeting was held in Brussels on 21-22 October 2014 (Scourse and Williams 2014).

The GAM minutes provide a good summary of the presentations and discussion on WP2 Steels. Consensus has been reached on the protocol for the leaching and/or corrosion experiments to be performed by various WP2 participants, notwithstanding the late discussion of whether to use $Ca(OH)_2$ or NaOH solutions to simulate the alkaline cementitious pore water. There seems to be sufficient effort planned for determining the ^{14}C release rate, with a smaller number of corrosion tests planned to measure the corrosion rate under the simulated repository conditions. The latter measurements are important if the congruent release hypothesis is to be validated, which would be an important contribution to the development of a mechanistically based ^{14}C source-term model. It is to be expected that some mechanistic information should inevitably be forthcoming from such leach/corrosion tests, although no specific mechanistic studies appear to be planned. There still appears to be some uncertainty regarding the question of the ^{14}C inventory, with tests planned to check calculated inventories against measured values, although there is little apparent existing or planned work to determine the distribution and chemical nature of the ^{14}C inventory.

In conjunction with WP2, there is significant effort being devoted to the development of analytical techniques in WP3 Zircaloy. This effort will assist in the determination of the rate of release of ^{14}C from steels and Zircaloy, as well as provide some mechanistic information. As a minimum, the procedures being developed will indicate whether the ^{14}C is released in the gaseous or dissolved forms and whether the dissolved species are inorganic or organic in nature. The review of existing information on the release of ^{14}C from Zircaloy suggests that much of the inventory is present in the oxide, although the minutes suggest that it will not be possible to distinguish these two sources in the planned experiments. If correct, this is unfortunate, as the release rates from the oxide and the metal (and, hence, how these releases are simulated in the ^{14}C source term model) could be quite different, a fact which would ideally be reflected in the source-term model. In the absence of such new mechanistic information, it would be necessary to rely on a congruent release model but, since the rate of Zr corrosion in alkaline solution is so low, such a model might not be conservative if there is a more-rapid release mechanism of ^{14}C from the oxide. Continued experimentation should indicate whether this is the case.

The work package on ion-exchange resins (WP4 Ion-exchange Resins) is well-focussed and appears to have access to a large number of relevant samples, although the extent of existing knowledge in the literature is stated to be less than for the other waste forms. The potential for time-dependent changes in the structure of the resins, and the consequences for ^{14}C release, are recognized and some of the partners will investigate this possibility.

In contrast to some of the other waste form types and work packages, the work package on graphite (WP5) will benefit from a significant existing database from earlier related projects. This wealth of existing information will, perhaps, allow greater mechanistic insight to be developed within the CAST project. For example, one partner is planning to examine the structure and chemical composition of the graphite and another will examine the spatial distribution of ^{14}C within the waste form. There is also existing information on the rate and mode of ^{14}C release from irradiated-graphite (i-graphite), which takes the form of a rapid initial release followed by a lower steady-state release rate. There is also information available about the speciation of released ^{14}C, with an interesting observation of a 2:1 VOC[1]:CO release ratio under anaerobic conditions, but a 1:1 ratio under aerobic conditions. This wealth of existing information should enable WP5 to be able to delve into the details of the mechanisms of ^{14}C release from i-graphite to a greater extent than is possible for the other waste form types.

Activities in WP 6 Safety Case will not get fully under way until models and data become available from the four waste-form-related work packages. Nevertheless, planning is well in hand for the safety assessments, with realistic schedules having been provided to the partners in WP2, 3, 4, and 5 for the provision of models and data.

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[1] Volatile organic carbon

Work Packages 1 and 7, on project co-ordination and dissemination respectively, appear to be well in hand at this stage of the project.

2.3 D2.2 WP2 Steels Annual Report – Year 1

The WP2 annual report describes progress made in 2014 on three tasks (Mibus et al. 2015):

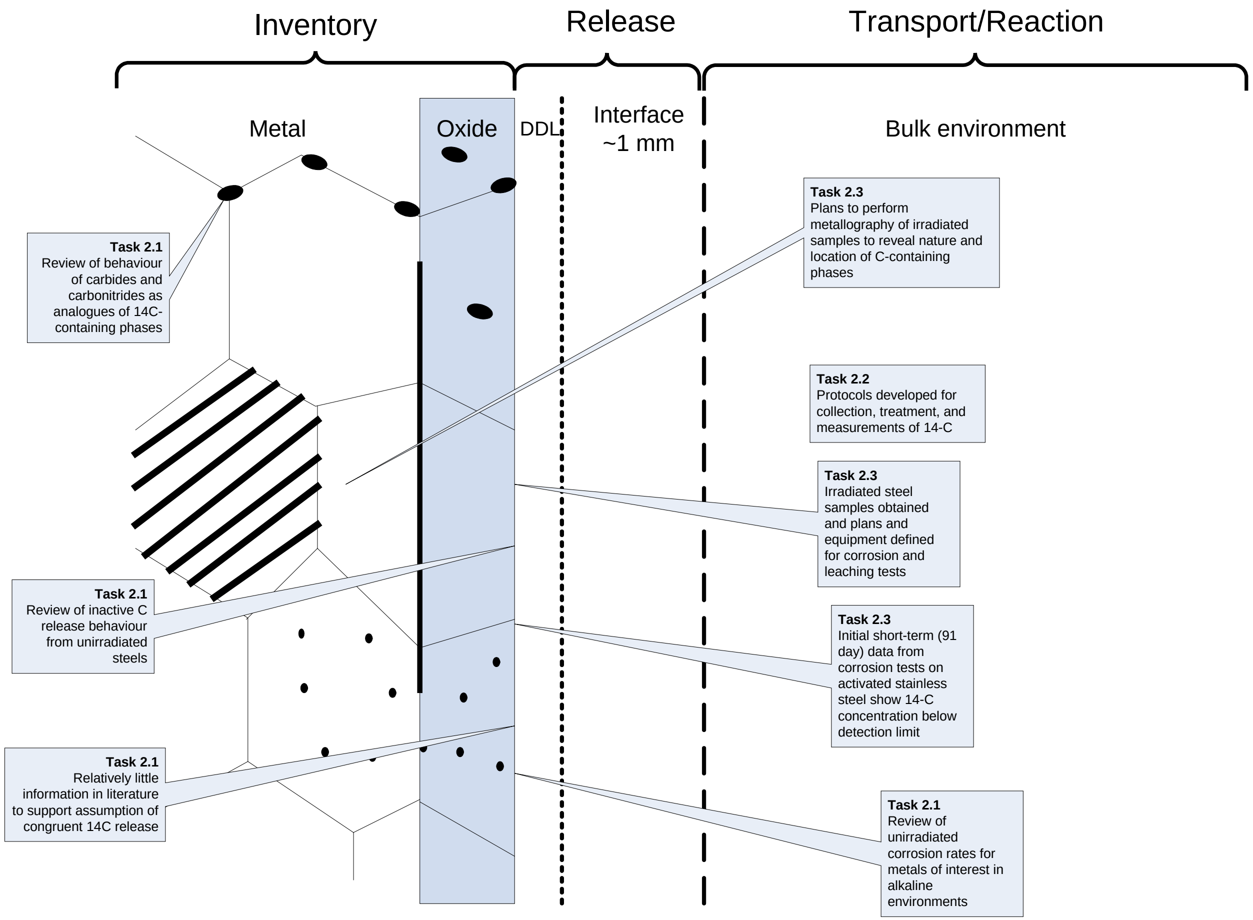
- Task 2.1: Literature review;
- Task 2.2: Development of analytical methods for measuring ^{14}C speciation;
- Task 2.3: Corrosion experiments and measurement of released ^{14}C.

The areas in which the 2014 activities have contributed to an improved understanding of the overall ^{14}C source term for steels are highlighted in Figure 2 and described in more detail below.

2.3.1 Task 2.1: Literature review

A detailed literature review on the release of ^{14}C from steels was completed and published during the year (Swanton et al. 2015). The highlights from the review include:

- A summary of the corrosion rates of carbon and stainless steels in alkaline conditions;
- A review of the limited available information of the ^{14}C inventory in irradiated steels, especially with respect to the physical distribution and chemical nature;
- A description of the dissolution behaviour of carbides and carbonitrides as possible inactive analogues of ^{14}C-containing phases in irradiated steels;
- A review of the characteristics of the release of inactive C from the corrosion of steel;
- A description of the single reported study of the release of ^{14}C from irradiated steel.



Task 2.1
Review of behaviour of carbides and carbonitrides as analogues of 14C-containing phases

Task 2.3
Plans to perform metallography of irradiated samples to reveal nature and location of C-containing phases

Task 2.2
Protocols developed for collection, treatment, and measurements of 14-C

Task 2.3
Irradiated steel samples obtained and plans and equipment defined for corrosion and leaching tests

Task 2.1
Review of inactive C release behaviour from unirradiated steels

Task 2.3
Initial short-term (91 day) data from corrosion tests on activated stainless steel show 14-C concentration below detection limit

Task 2.1
Relatively little information in literature to support assumption of congruent 14C release

Task 2.1
Review of unirradiated corrosion rates for metals of interest in alkaline environments

Figure 2: Summary of Progress in Developing a ^{14}C Source Term for Steels in 2014.

The latter study is important as it provides some evidence (albeit with treated, oxide-free samples) in support of the assumption of the congruent release of ^{14}C. Congruent release is currently the default assumption used for the ^{14}C source term in a number of safety assessments. Further experimental evidence for congruent release would be a useful outcome of the CAST project.

2.3.1 Task 2.2: Development of analytical methods for measuring ^{14}C speciation

The sampling and analysis of ^{14}C in leachates from experiments with irradiated materials is clearly a challenge, primarily because of the low concentrations of ^{14}C expected to be released over experimental timescales. The development of analytical procedures within the CAST project is a joint effort between WP2 and 3.

Protocols have been developed for the sampling, preparation, and analysis of ^{14}C from leachates and gas samples from corrosion and leaching experiments. These protocols account for the need to sample for both organic and inorganic ^{14}C-containing species. From the evidence available to date, it would seem that low molecular weight organics are the predominant form to be expected in tests.

Some initial results from corrosion tests on irradiated and unirradiated samples suggest that the concentration of ^{14}C will be very low, so more-sensitive analytical procedures such as accelerator mass spectrometry (AMS) may be required.

Based on the progress made to date, it appears as if appropriate sampling and analytical techniques will be in place in time for use in the various corrosion and leaching studies planned in the different WP.

2.3.2 Task 2.3: Corrosion experiments and measurement of released ^{14}C

In terms of the corrosion testing, the year under review has been one of sample collection and the development of experimental plans. All organizations involved have either received irradiated samples or have plans in place. Some are in the process of purchasing and assembling the necessary experimental apparatus. There was an ongoing discussion about the most appropriate test solution to use, but there seems now to be a consensus that NaOH should be used to simulate the alkaline cement pore water instead of $Ca(OH)_2$ in order to avoid the precipitation of ^{14}C-containing carbonate phases, which would otherwise further reduce the amount of ^{14}C in the leachate.

One organization has started corrosion experiments on irradiated stainless steel and has preliminary data after 91 days exposure. To date, the amount of ^{14}C released to solution is below the detection limit, highlighting the analytical challenges that the project faces.

One or two of the organizations intend to conduct metallography on the irradiated samples. Metallography is a useful method for identifying and locating C-containing phases in steels and it is recommended that all organizations should perform metallography in order to supplement the limited database on the nature and distribution of ^{14}C-containing phases in irradiated materials.

2.4 *D3.5 WP3 Zircaloy Annual Report – Year 1*

The WP3 annual report describes progress made in 2014 on three tasks (Necib et al. 2014):

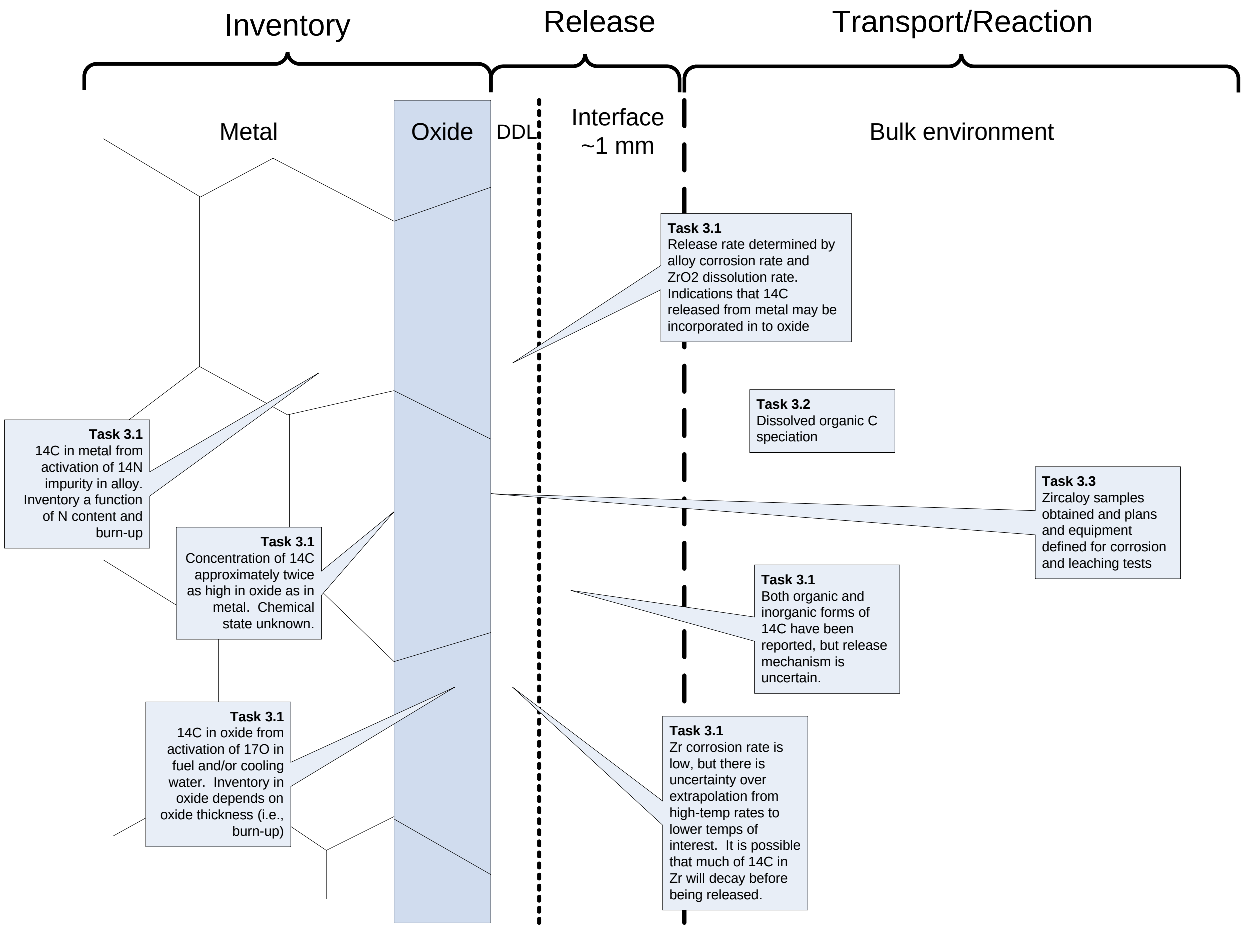
- Task 3.1: State-of-the-art review
- Task 3.2: Development of analytical methods for measuring ^{14}C speciation
- Task 3.3: Characterization of ^{14}C released from irradiated zirconium fuel clad wastes

The areas in which the 2014 activities have contributed to an improved understanding of the overall ^{14}C source term for Zr are highlighted in Figure 3 and described in more detail below.

2.4.1 Task 3.1: State-of-the-art review

The state-of-the-art review has provided useful information for the development of a ^{14}C source-term model for Zircaloy cladding, including:

- The major source of ^{14}C in the metal is the activation of ^{14}N impurities naturally present in the alloy. The inventory of ^{14}C from this source depends on the N content of the alloy and the fuel burn-up.
- The major source of ^{14}C in the oxide is from the activation of ^{17}O from the oxide fuel or from the cooling water. The ^{14}C concentration in the oxide is approximately twice that in the underlying metal, implying that ^{14}C released by corrosion of the Zircaloy may be incorporated in to the oxide and not released directly to solution.
- The chemical state of the ^{14}C in the cladding and oxide is unknown.
- There are two aspects to the release of ^{14}C from cladding; first corrosion of the cladding itself and second dissolution of the oxide.
- It is possible that the rate of release of ^{14}C from the metal and/or oxide will be so low that the ^{14}C will have decayed before being released in significant amounts to the environment.
- Whilst there is a lot of information about the rate and mechanism of Zircaloy corrosion at elevated temperature, it is difficult to extrapolate those findings to the lower temperatures of the repository. There is little available information on the dissolution rate of ZrO_2.



Task 3.1
Release rate determined by alloy corrosion rate and ZrO2 dissolution rate. Indications that 14C released from metal may be incorporated in to oxide

Task 3.2
Dissolved organic C speciation

Task 3.1
14C in metal from activation of 14N impurity in alloy. Inventory a function of N content and burn-up

Task 3.3
Zircaloy samples obtained and plans and equipment defined for corrosion and leaching tests

Task 3.1
Concentration of 14C approximately twice as high in oxide as in metal. Chemical state unknown.

Task 3.1
Both organic and inorganic forms of 14C have been reported, but release mechanism is uncertain.

Task 3.1
14C in oxide from activation of 17O in fuel and/or cooling water. Inventory in oxide depends on oxide thickness (i.e., burn-up)

Task 3.1
Zr corrosion rate is low, but there is uncertainty over extrapolation from high-temp rates to lower temps of interest. It is possible that much of 14C in Zr will decay before being released.

Figure 3: Summary of Progress in Developing a ^{14}C Source Term for Zircaloy Cladding in 2014.

2.4.2 Task 3.2: Development of analytical techniques

The work on developing analytical techniques for ^{14}C is progressing. There are plans to determine the detailed speciation of dissolved organic carbon.

2.4.3 Task 3.3: Characterization of ^{14}C released from irradiated zirconium

Plans for work on the measurement of ^{14}C release and Zircaloy corrosion progressed in 2014. The various European partners have identified (and, in most cases, collected) irradiated and non-irradiated Zircaloy samples in preparation for the start of testing in 2015. Furthermore, in many cases, apparatus has been commissioned and test conditions defined. Some partners are not as well advanced, but progress is expected by all participants in 2015.

In addition to ^{14}C leach tests, corrosion rate measurements will be made by some partner organizations. The two sets of measurements will indicate whether ^{14}C release is congruent with Zircaloy corrosion; a useful correlation (if shown to be correct) for safety assessment purposes. It is not clear, however, whether (a) there will be sufficient corrosion rate studies to identify such a correlation and (b) the proposed linear polarization resistance (LPR) and mass-change methods are sufficiently sensitive to measure the expected low rates of corrosion.

The European work is supplemented by data from ongoing leach tests from RWMC, Japan. These studies have shown different release rates from BWR and PWR fuel cladding.

2.5 *D4.2 WP4 Ion-exchange Resins Annual Report – Year 1*

Of the four tasks in WP 4, those for which progress was reported in the annual report (Reiller et al. 2014) were:

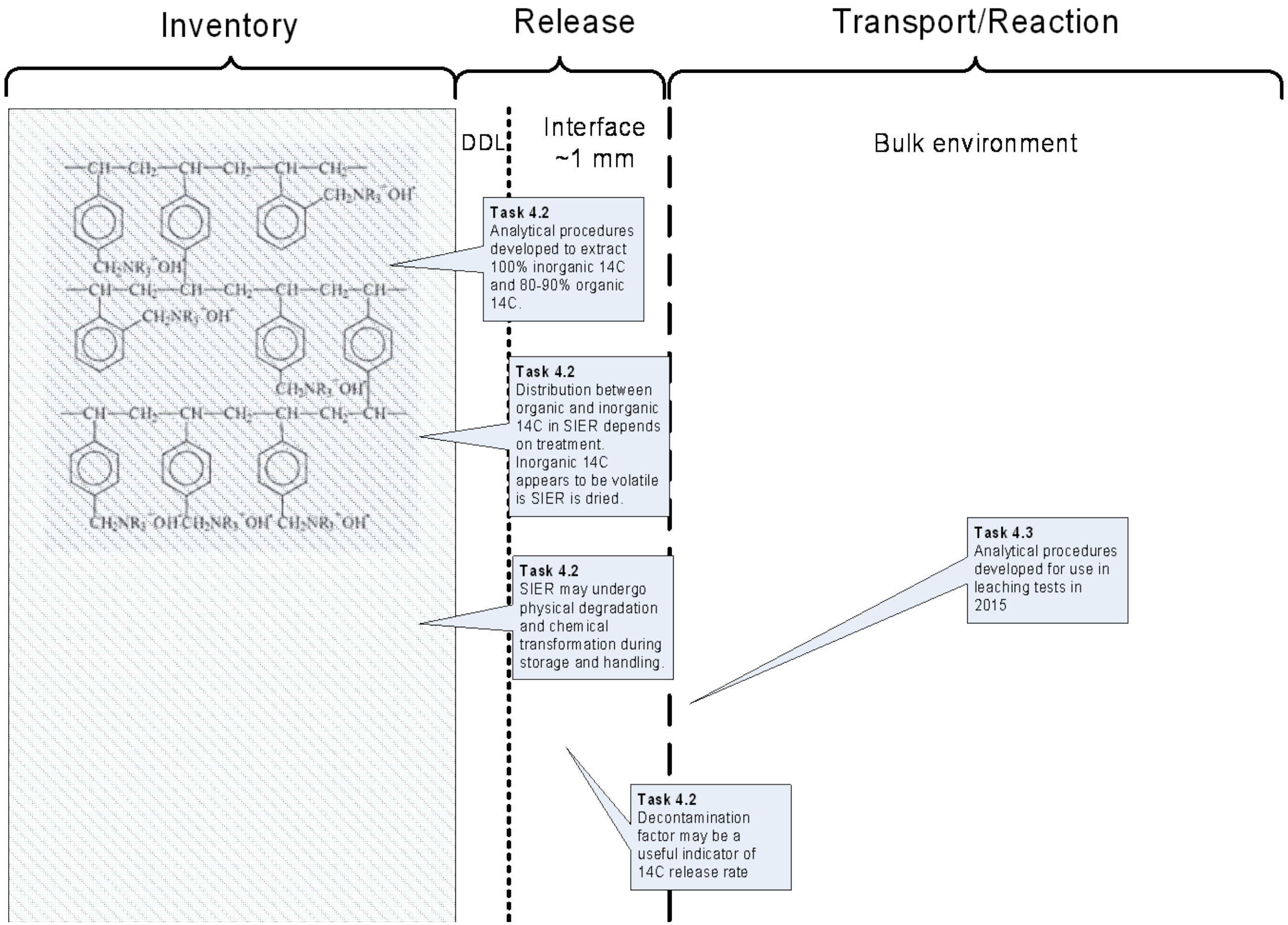
- Task 4.2: ^{14}C inventory and speciation in SIERS
- Task 4.3: ^{14}C release from SIERS and its speciation

The areas in which the 2014 activities have contributed to an improved understanding of the ^{14}C source term for SIER are highlighted in Figure 4 and described in more detail below.

2.5.1 Task 4.2: ^{14}C inventory and speciation in SIERS

All partners in Task 4.2 have identified and, in many cases, obtained samples of SIERs for subsequent characterization and testing.

Development of analytical and sampling procedures was accomplished in 2014, with the conclusion that up to 100% of the inorganic ^{14}C fraction could be recovered, along with 80-90% of the organic ^{14}C inventory. It is planned to speciate the organic fraction (in terms of the predominant functional groups, e.g., carboxylic acids, aromatics, ketones, alcohols, etc.). The distribution of organic and inorganic fractions appears to be a function of how the SIER is treated, with wet resins from various Swedish NPPs showing between 1-29% organic, but dried samples exhibiting an organic fraction as high as 90%. It appears, therefore, as if the inorganic fraction (in the form of various carbonate/bicarbonate species) is volatile.



Task 4.2
Analytical procedures developed to extract 100% inorganic 14C and 80-90% organic 14C.

Task 4.2
Distribution between organic and inorganic 14C in SIER depends on treatment. Inorganic 14C appears to be volatile is SIER is dried.

Task 4.2
SIER may undergo physical degradation and chemical transformation during storage and handling.

Task 4.3
Analytical procedures developed for use in leaching tests in 2015

Task 4.2
Decontamination factor may be a useful indicator of 14C release rate

Figure 4: Summary of Progress in Developing a ^{14}C Source Term for Spent Ion-exchange Resins in 2014.

A database of inorganic/organic speciation in SIERs from facilities in various countries is being developed.

The decontamination factor (i.e., the ratio of the activity of the stream into and out of the IER bed) may be a useful indicator of the release of ^{14}C in the repository. The decontamination factor is influenced by a number of processes but is a measure of the degree to which the ^{14}C is retained by the SIER and, therefore, might be expected to be related to the release characteristics under disposal conditions.

Microscopic examination of SIER samples reveals a certain amount of degradation of the resin. It is unclear whether this degradation is a consequence of the storage or handling conditions and, hence, whether such degradation would also be expected for disposed SIERs. However, since degradation of the SIER could impact the ^{14}C release behaviour, there are plans to investigate both the physical degradation and chemical transformation of SIERs.

2.5.2 Task 4.3: ^{14}C release from SIERS and its speciation

Studies on the release and speciation of ^{14}C from SIERs were planned in 2014. Analytical developments to improve the detection limit for dissolved and, especially, gaseous ^{14}C were undertaken. Leaching tests will begin on SIERs in 2015, as well as tests with γ-irradiated IERs loaded with non-active inorganic and organic carbon compounds to investigate the impact of γ-radiation.

2.6 *D5.2 WP5 Graphite Annual Report- Year 1*

Of the five tasks in WP5, those for which progress was reported in the annual report (Norris et al. 2015) were:

- Task 5.1: Review of CARBOWASTE and other relevant R&D activities
- Task 5.2: Characterisation of the ^{14}C inventory in i-graphite
- Task 5.3: Measurement of release of ^{14}C inventory from i-graphite

The areas in which the 2014 activities have contributed to an improved understanding of the ^{14}C source term for i-graphite are highlighted in Figure 4 and described in more detail below.

2.6.1 Review of CARBOWASTE and other relevant R&D

There is clearly a lot of useful and relevant information available from the earlier CARBOWASTE project that can be used for the CAST project. Other relevant prior studies include the CarboDISP project in Germany and UK NDA-RWMD studies on the characterisation and leaching of ^{14}C from i-graphite samples from Oldbury Magnox NPP. Specific examples of how this prior knowledge is informing and benefiting the CAST project include:

- ^{14}C leaching studies
    - In both liquid and gas phases, release rate decreases with time (by up to several orders of magnitude), followed by a slow long-term release rate.
    - More ^{14}C is released in the liquid phase than in the gas phase, with carbonates predominating in the liquid phase and CO and CH_4 in the gas phase. Both organic and inorganic C is released in the liquid phase.
    - Some labs report no obvious effect of the composition of the leachate on the ^{14}C release.
    - The mechanism of ^{14}C release is uncertain.
    - In UK tests, the VOC:CO ratio released is a function of redox conditions.
    - A fraction of the ^{14}C is present on the surfaces of and inside pores, due to the activation of adsorbed or entrained atmospheric $^{14}N_2$, and is relatively rapidly released.
    - In order to obtain an accurate ^{14}C inventory, ENEA developed an exfoliation and solvent extraction method for releasing ^{14}C in closed pores and intercalated between graphene layers.
- INR used results from CARBOWASTE data to predict the ^{14}C release rate for the TRIGA thermal column i-graphite, and is a good example of technology transfer in the CAST project.

- FZJ report that the ^{14}C inventory and release fraction poses some limits to the amount of waste that can be disposed of in the KONRAD facility. There may be similar limitations for other CAST-partner repositories.

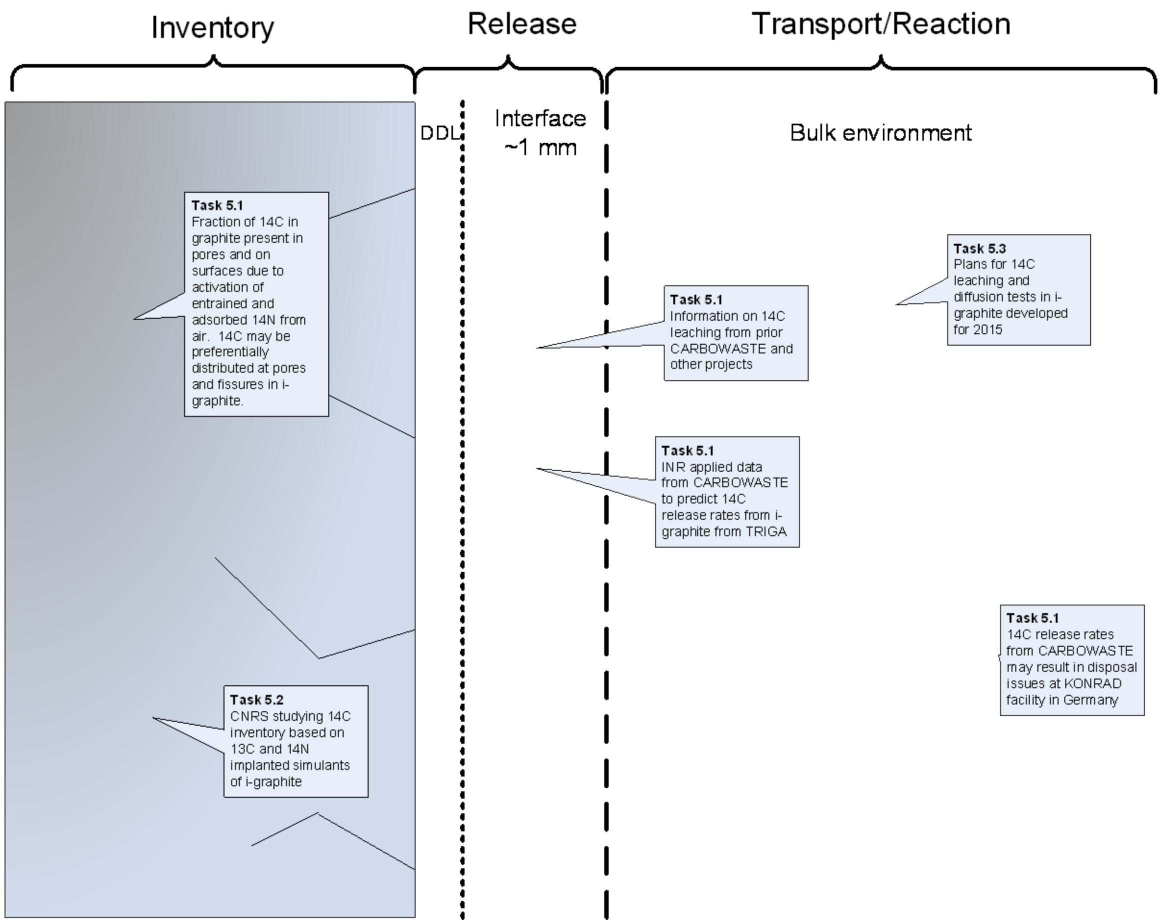


Figure 5: Summary of Progress in Developing a ^{14}C Source Term for Irradiated Graphite in 2014.

2.6.2 Characterisation of ^{14}C inventory in i-graphite

CNRS are carrying out basic research using ^{13}C and ^{14}N implanted in non-irradiated graphite in order to simulate the distribution of ^{14}C in i-graphite. These fundamental studies may provide insight into the nature and distribution of ^{14}C, as well as release mechanisms.

Other partners (e.g., IEG NASU, FZJ) are developing ^{14}C inventories for various i-graphite wastes.

2.6.3 Measurement of release of ^{14}C

The CAST partners are in various stages of preparation for ^{14}C leaching tests. Various organizations shared experimental plans and descriptions of test apparatus, including INR, FZJ, and CIEMAT. At this stage, however, there were no new leaching data to be reported, but progress is expected in 2015.

2.7 *Discussion and Conclusions*

The annual reports from the various WP demonstrate progress in all aspects of the CAST project. This first year of the project was clearly a period for designing and commissioning various sets of experimental apparatus, with the result that some partners were able to demonstrate more progress than others.

In terms of the overall aims of the CAST project, it is concluded that progress is being made in various areas to (i) better quantify and characterise the ^{14}C inventory of the different waste forms, (ii) develop suitable analytical procedures for measuring (the expected) low concentrations of ^{14}C, and (iii) disseminate knowledge between the various partners.

Because of the differing degrees of prior knowledge, there are differences in the current status of understanding for the various waste forms. For example, the extent of prior knowledge about the ^{14}C inventory (both in terms of the quantity and distribution) and release rates seems to be better for Zircaloy (WP3) than for i-graphite and, especially, SIER.

One area in which greater interaction may be beneficial is between the safety assessment analysis in WP6 and the experimentalists collecting data for the source term models in

WP2-5. Apart from information on the rate of release and the nature of the released ^{14}C, the safety analysts also need information on the possible reactions and transformations of ^{14}C in the near- and far-fields and within the biosphere. Thus, the transport of ^{14}C through the geosphere and biosphere is likely to be affected by a range of processes, including sorption, precipitation, microbial reactions, etc. It appears as if the safety analysts will rely on existing information and models to treat these processes, but there might be opportunities within the current experimental plans to further our understanding which could be usefully exploited within the CAST workscope.

Overall, progress is being made in all the areas reviewed.

3 Review of 2014 GAM Minutes and Year 1 Work Package Annual Reports by Dr. Irka Hajdas

3.1 *Introduction*

^{14}C production takes place in the atmosphere [LIBBY, 1946] where 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 naturally occurring, cosmogenic ^{14}C is fairly quickly oxidized and enters the global carbon cycle. The addition of anthropogenic ^{14}C takes place due to the production of bio-chemical tracers, in nuclear test (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 place between 1954 and 1964 AD [YIM, 2006]. Monitoring of operating nuclear power plants (NPP) allows the estimates of the local ^{14}C releases mostly as $^{14}CO_2$ and other gaseous forms [LEVIN ET AL., 1988, HUA ET AL., 2013].

The long-term storage and disposal of nuclear waste and ^{14}C releases has to be estimated. The reports of the first year activities of WPs in the CAST project summarize the published literature, outline the planned experiments and analytical development that are needed to quantify releases of organic and inorganic carbon from geological disposal facilities for radioactive waste.

3.2 *Review of Annual Reports Year 1 WP 2 – 5*

Annual reports of the first year of activities of the technical Work Packages 2, 3, 4 and 5 are reviewed with a focus on the planned ^{14}C activities analysis and analytical approach.

3.2.1 D2.2 WP2 Steels Annual Report – Year 1

12 participants were involved in following tasks:

1. Task 2.1 Review of literature

   a. Corrosion mechanisms and rates
   b. Release of ^{14}C and its speciation.
      i. Molecular forms of carbon in irradiated steels not clear
      ii. Possible interstitial carbide dissolved in the steel that forms methane hydrocarbons
      iii. Low corrosion rates <0.01µm/yr and even lower from Japanese studies
2. Task 2.2 Analytical methods developed for analysis at low concentration ^{14}C
   a. ^{14}Carbon speciation in liquid and gaseous phase
      i. GC and MS, HPLC
   b. ^{14}C analysis (concentration/activity)
      i. LCS and AMS in particular on gas samples (PSI)
3. Task 2.3 Corrosion studies and leaching experiments
   a. Corrosion experiment non-irradiated iron powders—studies of formation and release or organic compounds
      i. Acetic acid predominately formed among other carboxylic acids (oxalic, formic, malonic acids)
      ii. Methane dominated gaseous forms (other are ethane, propane, propene, butane)
   b. Leaching experiments of non-irradiated steels: Loviisa (Finland) and Japanese steel
      i. Simulated ground water composition
      ii. High TOC contents observed, possible contamination in preparation
   c. Leaching irradiated steels
      i. Stainless steel specimen will be studied by KIT-INE (no results reported yet)
      i. Autoclave under reducing conditions at ambient temperature using a dilute HF/H_2SO_4 mixture.
      ii. Follows procedure developed for ion exchange resins and process water of nuclear power reactors [MAGNUSSON *ET AL.*, 2008]

      iii. Separation of organic/inorganic forms from gaseous and liquid samples in 3-steps procedure (Fig.7.3&7.4 D2.2 Annual progress Report on WP2—Year 1)

d. Corrosion experiments under different conditions (pure water, alkaline and NaCl solutions) and different temperature (Japan).
    iv. Hydrogen release and absorption (gas chromatography)
        a. Corrosion rates low: At 720 days, the average corrosion rates at 303, 323 and 353 K were 7.7 10^{-4}, 2.6 10^{-3} and 7.5 10^{-3} µm/y, respectively
    v. Crevice corrosion—repassivation potential measurements E_{sp}
        a. Estimates of crevice corrosion possibilities E_{sp} lower than $E_{R,crevi}$ (threshold value) under most unfavorable conditions of temperature:353K, Cl^-:19000ppm
    i. Thickness of oxide layers 3 nm after 90 days at 323 K no changes observed

e. Planning corrosion experiments on non-irradiated and irradiated nitrogen rich steel (Belgium); system with outlet (argon purging): GC and HPLC for liquid
    vi. Static leaching tests
    vii. Accelerated corrosion tests
    viii. Metallographic analysis: grain size, grain orientation. Focus on carbide phase

3.2.2 D3.5 WP3 Zircaloy Annual Report Year 1

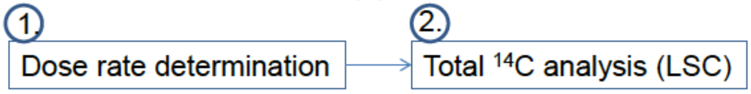
Participants have worked on Task 3.2 to determine possible analytical techniques to measure ^{14}C inventory and speciation.

1. Chromatographic separation is planned for identification of molecular composition. If required these molecules could be used for ^{14}C analysis.
2. An analytical strategy established in 2014 aims at collecting information on the size of molecules present in samples and semi-quantitative estimation of

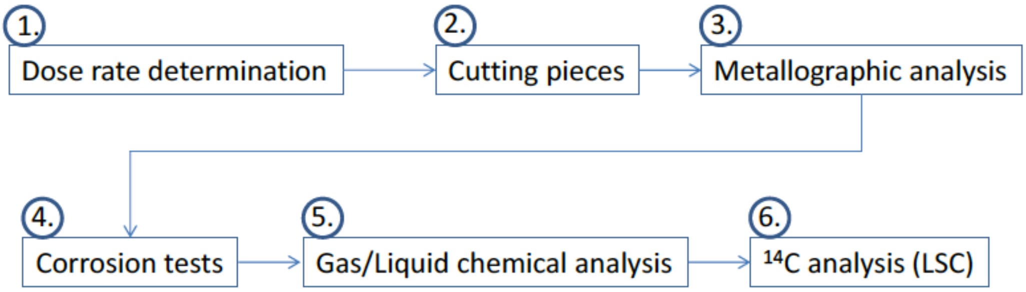
distribution of the different chemical families (alcohols, ketones, carboxylic acids, etc). Finally, the ultimate goal is to measure the ^{14}C concentrations.

3. NaOH leach planned as an alternative to $Ca(OH)_2$ that potentially can affect the ^{14}C inventory by precipitation of $CaCO_3$
4. Leaches in acidic media H_2SO_4/HF to estimate ^{14}C inventory for irradiated Zr4
5. Importance of nitrogen for production of ^{14}C however not always well known:
   a. ^{14}N in Zircaloys 30-40 ppm
   b. ^{14}C production calculated 30+/-10 kBq/g
6. Estimated corrosion rates: 1nm per year. For the 10 half-lives of ^{14}C 57000 yrs=114000 nm=0.57 10^4 x10^{-9}=0.57 10^{-5}=60 10^{-3} m
7. Chemical forms of ^{14}C released in leaching; Experiments for leaching planned with outlet for Liquid and Gas phase. Both organic and inorganic forms are present. However organic molecules such as carboxylic acids and alcohols are dominant. Identification of family of molecules is foreseen using infra red and ion chromatographic techniques (GS-MS, HPLC). There will also be possibility for trapping of carbon planned at the end of the identification (at SCK/CEN). Analytical methods for ^{14}C and carbon analysis: pre-concentration and GC-MS, GS-LSC. This is summarized in Figure 10 of REF CAST_D3.5 (Scheme of the experimental procedure for quantification of C-14 species of Zircaloy specimens) and in figure below (Fig. 32 of 1st Annual WP3 Progress Report (D3.5)).

(a)



(b)



8.
   Analytical techniques for measurement of the total ^{14}C content of leached are developed. Irradiated and not-irradiated Zr-4 samples. To catch the ^{14}C from the leaching corrosion cell and autoclaves were adapted to gas stripping and oxidation of organic C released. Corrosion cells for experiments and CO_2 will be collected from the autocalve--gas forms, purged N_2 and Ar, designed glove box-LSC set up (Numbers measured by SAKURAGI ET AL., (2013) are on the order of 10^{14} Bq total inventory, dependent on reactor type). For example detection limit for LSC given by [MAGNUSSON ET AL., 2008] is 0.4 Bq/kg**.** AMS analysis will be needed if the amounts of carbon are too low for LSC (GC or HPLC separation). It is not yet defined where the limit is.
9. Distribution of ^{14}C in metal/oxide film: almost all ^{14}C in metal, calculation show agreement with measured inventory in 740 µm of metal ca. 2.5 10^4 Bq/g (96.3% of total), rest in oxide layer.
10. Observation was made that non-irradiated samples corroded faster than irradiated once. Dependent if the samples were subject to neutron irradiation. Materials showed high variability in C-14 release rates after irradiation with fast neutrons.
11. Effects of alkalinity and temperature on corrosion rates investigated. Experiments with NaOH and simulated groundwater conditions (pH=12.5; after 90 days): acceleration of corrosion by factor 1.4 and 1.8, respectively, as compared to pure

water (1.3)

3.2.3 D4.2 WP4 Ion-Exchange Resins Annual Report – Year 1

This work package focuses on estimates of the potential contribution of ^{14}C from stored SIERs. From the outlined objectives the following has been reported as completed in year 2014:

1. Review of current status of knowledge of resins ^{14}C activity, analytical approaches in CAST deliverable D4.1
2. Analytical strategy developed:
    a. Sample preparation
        i. Leachates prepared in simulated cement conditions (NaOH solution
        ii. Estimates of radioactivity
    b. Mineralization and estimates of ^{14}C recovery on virgin ion exchange resins (IERs) spiked with ^{14}C-free carbonates or ^{14}C as glucose were performed by:
        i. Combustion
        ii. Acidification and wet oxidation (inorganic/organic carbon partition)

In both cases full (100% combustion and inorganic C) or nearly full recovery (81-91% wet oxidation of organic) was reported. Experiments will be repeated on real samples.

    c. Sizes and speciation of carbon bearing molecules using:
        i. Spectroscopic methods e.g. infrared analysis, FTIR for to identification of the main families of chemical functions such as carboxylic acids, aromatic compounds, ketones and alcohols.
        ii. Chromatographic methods:
            1. Ion and gas chromatography IC, GC combined with mass spectrometry MS for light molecules
            2. Development of electrospray-mass spectrometry technique for identification of large molecules
    d. Publication of these methods already applied for uranium carbide [LEGEND *ET AL.*, 2014].

3. Based on literature studies (D4.1) decontamination was identified as an important factor – subject of future research on physical-chemical properties of Ionic exchange resins (IERs) and their DF (decontamination factor)
    a. Morphology of fresh and old IERs
4. Preliminary gamma irradiation of IESs (Doses 0.1-0.5 MGy) for optimising: Equipment for gas sampling, Analytical approach and Concentration methods (note: this requires more precise definition)
5. Estimation of accumulation of total and organic ^{14}C in wet and dry resins shows that factors influencing the total activity in the waste are the process downstream of reactor, i.e. storage tanks and stirring (ventilation) where the inorganic ^{14}C can be lost.
6. Additional activities:
    a. Information on the ^{14}C cycle for basic training on 14C content in nuclear industries *ENEA-UTFISSM-POOO-016* (in English)

3.2.4 D5.2 WP5 Graphite Annual Report – Year 1

Source of ^{14}C from disposed irradiated graphites is at the focus of this work package. Main tasks are estimation of the inventory of ^{14}C in i-graphites, their release (long term storage) and possible ways of treatment.

1. Estimation of the inventory of ^{14}C
    a. Studies of location of ^{14}C in the graphite by applying irradiation and annealing of ^{14}N and ^{13}C implemented (200-300 nm depth) graphites. Irradiation with He^{2+}, Ar^{3+}, and S^{9+} for ^{13}C, to study gas radiolysis and irradiation effects as well as damage of graphite due to:
        1. Ballistic damage i.e. displacement of atoms (futures studies)
        2. Electronic excitation and ionisation due to radiation (beta, photons) as well as recoil atoms
            a. Displacement and release of ^{14}N
                i. Nitrogen migration towards the surface

            - ii. Formation of carbon nitride and other carbon compounds
            - iii. Irradiation and heat leading to loess of ^{14}N
        - b. Displacement of ^{13}C
            - i. No migration due to heat
            - ii. Reorganization of graphite structure, no ^{13}C release could be measured (technical problem)

2. Release (long term storage)
    - a. Estimates of i-graphite storage based on CARBOWASTE studies
        - i. Small amount of ^{14}C released (ca. 1%)
        - ii. Both organic and inorganic form released in alkaline conditions
        - iii. Amount of ^{14}C in liquid phase (as CO_2) larger than in gas phase (as CO and CH_4)
        - iv. Release decreasing in time with 1-2 order magnitude
        - v. Atoms of ^{14}C created in graphite form simple hydrocarbons and nitrogen compounds [CARLSSON ET AL., 2014]
    - b. Simulated releases in base environment: starting activity 1000 Bq/g
        1. Liquid phase of ca 2 Bq
        2. Gas phase 0.5 Bq
    - c. Separation of organic/inorganic form
    - d. Release of ^{14}C from treated graphite for estimation of total ^{14}C inventory for stored waste:
        - i. Importance of treatment for keeping the release as low as possible (<1%) for estimated storage volume
    - e. Measured cumulative activities of $^{14}CO_2$, ^{14}C O and $^{14}CH_4$ released to the gas phase at 7 different leaching conditions (powdered graphite, oxic/unoxic, pH 7/13, ambient/ high temp. 50ºC) of i-graphites (starting activity 84±11 kBq/g)
        - i. Fast release at the beginning of the leaching process, except for powdered graphite—probably gaseous ^{14}C lost in crushing

        ii. Higher release on solid piece at ambient temperature, pH 7—probably inorganic dissolved and added to total
        iii. Baseline conditions (ambient temp., pH 13, solid piece, unoxic):
            1. Higher release at the onset of leaching 3 months (3 Bq/g)
            2. Release 3-12 months total 2 Bq/g,
            3. Mainly hydrocarbons/OC and CO (ratio 2:1) and less than 2% as CO_2
        iv. Possible difference in release due to different types of graphite

3. Treatment
    a. Testing exfoliation-like process on the graphite by organic solvents supported by sonication
        i. ^{14}C activity measured on ca. 0.12 g of sample: range 70-1500 Bq/g
        ii. Choice of solvents:
            1. N-Methyl-2-pyrrolidone (NMP)
            2. N,N-Dimethylacetamide (DMA)
            3. N,N-Dimethylformamide (DMF)
        iii. Sonication time and energy
        iv. Centrifuging
        v. Effectiveness of investigated with Raman spectrometry:
            1. DMF + sonication show increased disorder in the graphite sample
            2. Decreased thickness due to the minor layers with respect to the original graphite
        vi. Future work:
            1. ^{14}C activity from treated graphite in progress
            2. optimizing the method

    b. Leaching experiments
        i. Samples of graphite with ^{14}C activity ca. 1000 Bq/g chosen for leaching experiments
        ii. Testing storage under ‘humid conditions’
        iii. Accelerated leaching experiment (expected higher 14C concent. In leachate)
        iv. ‘harsh’ leaching (soxhlet extraction)
        v. Leaching products: gas and liquid phase for identification by planned

GCMS analysis.

3.3 D1.4 CAST 2nd General Assembly Meeting Minutes

Each of working packaging presented updates on progress of the last year.

WP2 Steels Update: Task 2 analytical development --well underway, Task 3 corrosion experiments was planned in Oct2014.

Two sets of Round Robin comparisons are planned: activation calculations in steels and possibly C-14 speciation measurements at (PSI, Armines)

During a joint WP2/WP3 technical meeting Paris July 2014 corrosion tests were planned. Another joined meeting to be organized at PSI in April 2015 should establish the analytical procedures.

Steve Swanton from Amec presented the overview of literature: corrosion and release of carbon-14 might be not fully understood including the effects of irradiation on the metal structure. Future results of WP2 are very important for clarification of these issues..

Experimental Set-Up, PSI. Very low carbon content requires addition of carrier (dead carbon):

1. Liquid phase to gas phase [FAHRNI ET AL., 2010]. Here they used LC to separate dicarboxylic acids for CSRA. It would be interesting to see what chemical species we have here from irradiated steels.

2. testing this approach to corrosion studies (gas phase).

WP3 Zircaloys--analytical developments similar as for steels. WP2 and 3 joint meeting at PSI, common developments. Zircaloys: here difficulty to distinguish between metal and oxide as a source of ^{14}C. First step is to estimate the total inventory.

WP4 Ion-Exchange Resins: not much research carbon-14 and on ion-exchange resins has been published.

Partners should rely on collaboration with AMS facilities. Cavity ring-down spectroscopy for ^{14}C analysis -- quite new technique. Not much data exist. The first results show that required is 70 mg of carbon [GALLI ET AL., 2013].

Inventories of ^{14}C in SIERS will investigate the degradation of structure using SEM, AFM, FTIR and XRF. CEA/LARC reports development for separation total ^{14}C and inorganic ^{14}C. Organic still requires development. ENEA developed double combustion. Meeting of WP4 planned beginning of 2015.

WP5 i-graphites: RWM knowledge from CARBOWASTE will be integrated into the present project.

ENEA: Treatment proposed --extraction of ^{14}C with organic solvents. Use of AMS considered by IFIN-HH and FJZ when concentration less than 1%.

The treatment of graphite and what impact it has on release of gaseous ^{14}C was discussed. From the CARBOWASTE results it is evident that redox conditions are important for the ratios hydrocarbon/CO.

WP6 safety case context: a document D6.1 (^{14}C in safety assessments) was in preparation and was planned for peer review within the WP6 group. Planned for June 2015. Important issue is the transport of gaseous ^{14}C (different concepts exist, document should explain why).

3.4 *Conclusions and Recommendations*

The activities undertaken in all Work Packages in the first year of CAST project focussed on: reviewing available literature, planning experiments and methodological development. Some experiments were performed and first results are available, however most are in the planning phase. Most of the measurements of ^{14}C activities use LCS with some clear indication for a need to use AMS facilities. Here, the recommendation is to establish contact with AMS facilities prior to planning the experiments.

4 End-Users

The review comments from each of the end-user group representatives are summarised in the following sub-sections.

4.1 *Ondraf/Niras Review Comments*

Ondraf/Niras have focussed their review on WP2 and WP3, as these are the most relevant to their national waste disposal programme.

4.1.1 D3.5 WP3 Zircaloy Annual Report – Year 1

4.1.1.1 Remarks on Section 2.1 Andra contribution in D3.5

- Section 2.1.1, page 2: "*the calculation overestimates the inventory, even when the calculation is carried out with the actual value of the nitrogen content in alloy*". What is the extent of the overestimation?
- Section 2.1.2: Title should mention that it addresses both "hulls" of CSD-C and "claddings" of spent fuel assembly.
- Section 2.1.2.1, page 3: the higher (factor 2) 14C content in Zr oxide layers seems correlated to the corrosion mechanism (14C from corrosion of the bulk metal is retained in the oxide layer).
- Conclusions, page 54: In the conclusions, the higher 14C content in zirconia seems correlated to the activation of oxygen from coolant and fuel. This is confusing. For information: an additional experimental observation of a higher (up to a factor 4) 14C content in the external zirconia layer is given in report PNL-5109-105-UC-802: "Characterization of Spent Fuel Approved Testing Material-ATM-105" by R. J. Guenther et al. (1991).
- Section 2.1.2.1, page 4: "*Corrosion tests on pre-oxidized samples*": to what extent are pre-oxidized samples representative of irradiated Zr alloy? Is there a significant difference in oxidation rates between in-reactor and autoclave conditions?

4.1.1.2 Remarks on Section 2.3 CEA contribution in D3.5

- Table 1: is the initial (before irradiation) nitrogen concentration known (best estimate/maximal)?
- Are the initial (before the corrosion experiments) characteristics of the samples known: C-14 content in metal/oxide layer, thickness of the oxide layer…? If known, are these determined theoretically or experimentally?

4.1.1.3 Remarks on Section 2.4 INR contribution in D3.5

- Table 2: is the initial (before irradiation) nitrogen concentration known (best estimate/maximal)?
- Are the initial (before the corrosion experiments) characteristics of the samples known: C-14 content in metal/oxide layer, thickness of the oxide layer…? If known, are these determined theoretically or experimentally?

4.1.1.4 Remarks on Section 2.7 RWMC contribution in D3.5

- Figure 20: the lines for the approximate equations at lower values for Time are close together. What are the error margins on the corrosion rate? Do they allow any comparison with the approximate equations at these lower values for Time?
- Figure 23/24: these figures are not easily readable due to overlap of the data points. The same issue applies to some other figures in this chapter.

4.1.2 D4.2 WP4 Ion-Exchange Resins Annual Report – Year 1

What are the possible physical and chemical alterations of the SIERs due to conditioning of the waste (homogeneous cementation of the resins)? Will the conditioning method, like the storage conditions, change the behaviour of the waste in a geological repository (speciation, leaching rate…)?

4.2 *RWM Review Comments*

At the current stage in the United Kingdom (UK) Government programme to manage radioactive wastes, a preferred site for a Geological Disposal Facility (GDF) has not been identified. Therefore, any safety assessments produced as part of an overall safety case are at a ‘generic’ stage. We call it a generic safety case because it must cover a range of possible disposal environments and facility designs. Nevertheless, this work builds on more than 25 years of experience studying geological disposal and undertaking safety assessments in the UK. It also draws on the extensive body of knowledge and experience in other countries gained through overseas radioactive waste management programmes.

The current focus of the UK programme on carbon-14 is on release via the gas pathway. We only have a small inventory of ion exchange resins and zircaloy, so at this stage our focus in on carbon-14 in graphite and steels. RWM has decided to adopt a collaborative approach to tackling issues related to carbon-14 by establishing an Integrated Project Team, in which the partners work together to address all aspects of the issue [NDA, 2012]. The overall aim of this integrated project is:

“To support geological disposal of UK wastes containing carbon-14, by integrating our evolving understanding from current and pre-existing projects, in order to develop a holistic approach to carbon-14 management in the disposal system”

The first phase of the work of the integrated project team has shown, however, that there is considerable scope for reducing the calculated radiological consequence for these wastes. Important waste materials that contain carbon-14 in the UK context are irradiated reactive metals, irradiated steels and irradiated graphite. Work within CAST will address the latter two types of waste materials under WP2 and WP5. Both these work packages appear to be progressing in a satisfactory manner and should add valuable information to our understanding.

4.3 GRS Review Comments

These comments relate to the work performed in the CAST work packages WP2 and WP3 on the release of C-14 from irradiated steels and Zircaloy and its use for future safety cases in the German programme. The reason not considering the other WPs at the moment is that the waste types regarded there are classified as waste types with negligible heat generation in Germany, which are foreseen to be disposed of in the already licensed and currently constructed repository Konrad. Safety assessments for the Konrad site are currently not performed.

The latest major safety assessment for a nuclear waste repository for heat-generating waste in Germany was the Preliminary Safety Analysis for Gorleben performed from 2010 to 2013. The radiological consequence analysis as part of the safety assessment has shown that in the reference case, an early release of C-14 in the gas phase is the most relevant radionuclide for the radionuclide flux out of the repository with calculated values close to the regulatory limit [Larue et al. 2013]. This C-14 stems from both irradiated steels and Zircaloy from directly disposed burnt up fuel elements. Due to uncertainties in the C-14 release behaviour from the waste, conservative assumptions have been made. The result of these conservative simulations shows the need for additional research and development to reduce potential uncertainties and conservatism. The calculated C-14 fluxes highly depend on the assumptions regarding the release time and the chemical form of the C-14 in and released from irradiated steels and Zircaloy. Therefore, a high priority is to reduce the uncertainty on the release behaviour of C-14. This is mainly related to three questions:

1. What percentage of the C-14 present in the irradiated steels and Zircaloy can be released into volatile form?
2. What is the temporal behaviour of the release?
3. Is liquid water necessary to transfer C-14 into volatile form or does this also occur in the presence of air humidity or even completely without the presence of liquid water or humidity?

From the CAST work descriptions provided, the first year of work in the CAST project was mainly devoted to collection and review of the state of the art and to the planning and setting up of the experimental work, including development of new analytical techniques.

The reviewed work in both work packages WP2 and WP3 are both very useful pieces of work, as existing information has not been collated in a coherent way before. The collated information shows that there are still high uncertainties in many questions, or even contradicting results.

The designated experiments described in the work package descriptions are promising to reduce this existing uncertainty. A remarkable effort has been undertaken already to provide the analytical requirements that the experiments can be carried out successfully. The experiments seem to be well planned and to have the needed sensitivity to measure significant results. Regarding to the three questions given above, the designated experiments seem to be suitable to reduce the uncertainty for the first two topics.

All experiments seem to be planned investigating corrosion of the samples in liquid water as release process of C-14 from the irradiated material. Therefore, no information is expected from the experiments to contribute to the answer of question three given above.

In Germany there is still no decision made regarding the host rock of a future repository for heat-generating waste. Rock salt, clay rock and crystalline rock are under consideration. From the descriptions provided, it seems that the chemical conditions planned to be used in the experiments are suited best to the chemical conditions expected in a repository in clay host rock. The actual use of the results for repositories in crystalline rock or even salt rock cannot be judged at the moment due to different chemical conditions to be expected.

In summary after the first year it can be concluded that the CAST project is in a very good perspective to produce results that are useul in the national context. However, not all the open questions existing can be expected to be solved by one single project.

4.4 *LEI Review Comments*

4.4.1 D2.2 WP2 Steels Annual Report – Year 1

The main objective for Work Package 2 (WP2) is identification and quantification of ^{14}C species formed during corrosion of irradiated steels. From the General Assembly minutes - Year 2 it is evident, that outcomes from the work performed in WP2 will be useful for the safety case. The activities of the WP2 include:

- State of the art review of steel corrosion and ^{14}C release;

- Experiments with activated steel (measurements of corrosion rate and estimation of ^{14}C fraction in liquid and gas phases).

The literature review has already been completed and the report has been released. The review presents the current state of understanding of steel corrosion rates and ^{14}C releases from irradiated steels under conditions relevant to the storage and long-term disposal of radioactive wastes.

The experiments with activated steel are planned to be performed for the conditions close to the repository conditions as well as under near-neutral conditions. Impact of samples' structure, geometry and experiment duration on the overall conclusion of the measurement results (of corrosion, leaching, speciation experiments) should also be addressed. The uncertainty range of experimental measurements needs to be indicated as well.

It is expected that the output of the activities in WP2 will provide valuable information, which could serve as a firm basis for substantiation of decisions and assumptions made in the safety case regarding source term and ^{14}C release rate.

4.4.2 D3.5 WP3 Zircaloy Annual Report – Year 1

Work Package 3 (WP3) is related to Zircaloy and Zr alloys in the CAST project. It aims to obtain a better understanding of ^{14}C behaviour in waste Zr fuel claddings under disposal conditions with regard to ^{14}C inventory (and origins), release from waste packages and speciation of released ^{14}C. The activities of the WP3 include:

- Literature review (released as delivery D3.1) on the State of the Art of ^{14}C in Zircaloy and Zr alloys.
- Analysis of the total ^{14}C content in the irradiated Zr alloys as well as its fraction in the liquid and gas phases.
- Analysis of distribution of ^{14}C between metal and oxide layer.

- Leaching experiments for determination of organic/inorganic ^{14}C fraction and speciation of organic ^{14}C.
- Measurements of corrosion rate.

The literature review presents available information on the inventory and distribution of ^{14}C in Zircaloy cladding, release rate of ^{14}C from Zircaloy hulls and chemical forms of ^{14}C released.

Experiments on total ^{14}C content in the irradiated Zr alloys and its fraction in the liquid and gas phases as well as distribution of ^{14}C between metal and oxide layer are ongoing and some short term results are available, but the tendency should be checked using longer term test data.

Leaching experiments for determination of organic/inorganic ^{14}C fraction are planned and speciation of organic ^{14}C will be investigated. It is foreseen to conduct leaching experiments for estimation of the ^{14}C release from irradiated Zr alloys in water representative of cement environment, which corresponds to the repository conditions.

It is expected that quantification of gaseous and dissolved ^{14}C species as well as total content of ^{14}C will be useful for defining the source term in the safety analysis. Quantification of ^{14}C between metal and oxide layer is very important for the safety case as release mechanism in both cases is different.

It is expected that based on the experiments performed in WP3 it would be possible to distinguish organic ^{14}C fraction in the inventory and to produce more realistic safety case.

The mechanism and the rate of ^{14}C release from hulls are supposed to be controlled largely by the uniform corrosion rate of Zircaloy. The absence of pitting corrosion effect would support the assumption that cladding material contributes to retardation function of ^{14}C. Therefore, the corrosion experiments that are going to be performed in WP3 are of high importance.

There are two RBMK reactors in Lithuania where Zr alloys E110 and E125 are used. As most experiments are, or will be, performed with different type of Zr alloys, the outcomes from WP3 should be used with care. The planned experiments with irradiated and unirradiated Zr alloys will cover a wide range of conditions and provide valuable information which could be used in the safety case. It is expected that impact of samples' structure, geometry and experiment duration on the overall conclusion on the measurement results (of corrosion, leaching, speciation experiments) will also be addressed. The uncertainty range of experimental measurements should also be indicated.

4.4.3 D4.2 WP4 Ion-Exchange Resins Annual Report – Year 1

The aim of Work Package 4 (WP4) is dedicated to the study of speciation, source term, leaching, and gaseous release of ^{14}C from spent ion exchange resins (SIERs). The activities of the WP4 include:

- Literature review (released as delivery D4.1).
- Experiments for determination of organic/inorganic ^{14}C fraction and speciation of organic ^{14}C.
- Investigations on degradation of the IER.
- Investigations on the release of gaseous ^{14}C from SIERs.
- Identification of processes/parameters the most influencing ^{14}C release from SIERs.

The state of the art review on sample choice, analytical techniques and current knowledge of release from spent ion-exchange resins has already been performed. It was recognized that there is only scarce information about the release and speciation of ^{14}C originated from SIERs. No published investigations on the release of gaseous ^{14}C from SIERs have been found. Therefore, all investigations on SIERs conducted in the WP4 will be of the great value.

A number of experiments are going to be performed in WP4 in order to estimate total ^{14}C activity and its distribution among inorganic and organic form, distribution of organic ^{14}C among the different chemical families. Some results on activity of SIERs from BWR and PWR systems and distribution among organic/inorganic form are already presented.

The experiments of ^{14}C speciation on SIERs and released by SIERs are going to be performed in different conditions. This would enable to evaluate the most influencing processes/parameters such as e.g. radiolysis, mixed disposal, degradation, rehydration, pH, etc. and provide information for the safety case on which point the most attention should be paid and which source term related parameters might have significant impact on the overall performance of the disposal system.

It is expected that the experiments on ^{14}C speciation performed in WP4 will serve as a good background in determination of the source term, which will be used in the safety case.

Outcomes of experiments dedicated to the degradation of the IER will provide information about the degradation of the physical structure and the chemical transformation of the resins due to storage conditions, what is also important information for the safety assessment.

As no published investigations on the release of gaseous ^{14}C from SIERs have been found, investigations on the generation of gases during storage and degradation of SIERs will be of high importance.

There is a certain amount of SIERs from RBMK reactor system in Lithuania. They are cemented and are going to be disposed of in a near surface repository. The output from the activity in WP4 will be very important when performing the safety assessment as the obtained information will provide a better understanding of the ^{14}C source term from spent ion exchange resins of different origins and likely release and chemical species.

4.4.4 D5.2 WP5 Graphite Annual Report – Year 1

Work Package 5 (WP5) of the CAST project considers i-graphite and related ^{14}C behaviour. According to the Annual Progress Report D5.2, the outcomes of the work performed in the WP5 group will give better understanding of the factors determining release of ^{14}C from i-graphite under disposal conditions. The work will not concentrate only on geological disposal facilities, but include surface disposal facilities as well. The activities of the WP5 include:

- Estimation of total ^{14}C inventory and concentration distribution in the i-graphite.
- Estimation of ^{14}C release rate from the i-graphite, ratio of dissolved/gaseous ^{14}C and speciation.
- Investigations on i-graphite treatment impact on leaching.

A lot of experiments are planned in WP5 in order to complete the above mentioned tasks. Some experiments have already been performed, others are underway.

It is expected that investigations on ^{14}C inventory and concentration distribution in the i-graphite will be useful for evaluation of the source term for the safety assessment. Release rate of the ^{14}C from the i-graphite and speciation is one of the key points in the safety assessment, as organic and inorganic compounds can behave differently under the defined repository conditions. It is expected to obtain from the WP5 information on potential ^{14}C release to solution and in form of gas from i-graphite in contact with aqueous solutions as well as its distribution among organic and inorganic species.

Analysis of impact of i-graphite treatment to ^{14}C releases performed in WP5 will provide the basis for consideration of i-graphite treatment alternatives and possibilities to dispose i-graphite in the surface repository.

It should be noted that the results of the work performed in WP5 cannot be directly and simply applied to the specific needs as different types of i-graphite is used for analysis. Therefore, the type of i-graphite analysed should be clearly identified. In addition, when presenting the results of the investigations, it would be useful to get the range of input parameter values (e.g. amount of impurities in graphite) or graphite specific information for which the obtained results are expected to be valid. Impact of samples' structure, geometry and experiment duration on the overall conclusion on measurement results (leaching, speciation experiments) should also be addressed. Comparison of i-graphite leaching results under common conditions and release model is expected to form a basis for application in safety assessments.

There are about 3800 tonnes of the i-graphite in Lithuania and the way of disposal of the graphite waste is still under consideration. A good support to the final decision on disposal of i-graphite could give the safety assessment. In order to avoid over conservatism in the assessment and to provide good substantiation for the assumptions, the outputs from the WP5 is of high importance as input to the safety case.

4.4.5 Conclusions and Recommendations

The review of the activities of WP2, 3, 4 and 5 revealed that a lot of work has already been done by the participants. Based on the literature review and national programmes appropriate experiments and investigations are planned.

It is expected that the outcomes from the WP2-5 will provide valuable information to the safety assessment. However, the results of the investigations should be used with care as different types of materials as well as history in the reactors may occur. It is expected that the outcomes from researches performed by the WP2-5 in conjunction with WP6 will include recommendations how to apply the obtained results in the safety case.

4.5 *Surao Review Comments*

4.5.1 D2.2 - WP2 Steels Annual Report – Year 1

WP2 is undertaking the most relevant research for SURAO. WP2 can provide realistic data for releasing radionuclides from activated metal parts of structure materials of spent fuel assemblies and reactor core structures. The literature review summarised the available data very well. The planned ‘Round-Robin’ comparison of activation calculations of ^{14}C in steels is also very interesting for SURAO.

4.5.2 D3.5 WP3 Zircaloy Annual Report – Year 1

The reference concept of the Czech Republic is direct disposal of spent fuel assemblies. The most important data for SURAO from this WP is primarily the better estimate of possible instant release fraction (IRF) of ^{14}C in zirconium and an estimate of maximal corrosion rates of zirconium under repository conditions.

4.5.3 D4.2 WP4 Ion-Exchange Resins Annual Report – Year 1

Currently in the Czech Republic, spent ion exchange resins (SIER) from WWER reactors are planned to be disposed of in the near surface repository at Dukovany, but it is not excluded that some of the SIER will have to be disposed of in a Deep Geological Repository. Data obtained in WP4 can significantly contribute to regular updates of safety cases for the Dukovany repository and may inform decisions concerning the disposal of SIERs in a DGR. In particular, speciation results dividing SIER into organic and inorganic parts will be very interesting for SURAO.

4.5.4 D5.2 WP5Graphite Annual Report – Year 1

Almost no graphite waste was accumulated in the Czech Republic, so WP5 is of less interest for SURAO.

4.6 *SKB Review Comments*

4.6.1 D1.4 – CAST 2nd GAM Minutes

The general assembly minutes are well written and appear to reflect the content of the interesting discussions which took place during the meeting accurately. A short description of the status of the various deliverables and the work progress in each work package is presented. The organisation of joint meetings concerning a common issue (mainly development of analytical methods in this initial stage), with researchers from two or more different work packages, is appreciated and positive. The major added value of this type of large collaborative projects is the contribution in the increased understanding of the complicated repository processes by providing a forum for the joint discussion of complex issues by several research groups.

4.6.2 D3.5 WP3 Zircaloy Annual Report - Year 1

The report gives a summary of the work carried out by the participants during the first year. Most of the participants, e.g. CEA, Subatech, INR, JRC/ITU, SCK/CEN have carried out preparations needed to start the leaching tests, including development of analytical methods. The state of the art report is compiled and a summary is given in the annual meeting report. The state of the art report is an impressive and well written summary of the literature on the subject. Only RWMC reports experimental measurements during the first year, probably because of data obtained during their long term experimental programme initiated before the projects started. There is one thing which should be clarified better while presenting the RWMC results: how was the concentration of C-14 in the oxide film measured? The fact that it is reported as at least twice higher than that in the metal seems to be explained here by the production via O-17 in the oxide, and then released by diffusion in solid phase or oxide dissolution (p.3). Both release mechanisms are difficult to defend at the relatively low temperatures and absence of high flows both under the experimental conditions and in a repository. However, it is difficult to sort out which values are calculated and which are measured in this part of the report.

4.6.3 D4.2 WP4 Ion-Exchange Resins Annual Report – Year 1

In this work package it is stated that very little previous information on the subject exists in the literature, basically only a Ph. D. thesis. From this perspective, the work accomplished under the first year of CAST in this work package is already an important contribution. Most of the research groups report preparations for experiment start, with special emphasis in the development of analytical methods. The statement on p. 26 that the knowledge of the chemical form of C-14 is important is correct, however it seems as chemical equilibrium in C-H-O system is the only pathway investigated for the formation of organic compounds. A discussion of the main mechanism of C-14 production in water is missing: if O-17 of a water molecule is converted to C-14, probably a CH_2 or other carbon radical is produced, which in water would react further to give various organic compounds-are there published studies on such a processes? A suggestion for the analysis methods used is: most, if not all, methods discussed use different oxidants to oxidize the whole resin, together with the absorbed organic species and analyse the CO_2 produced. In this case the dominant part of carbon comes from the resin itself and one could increase the sensitivity of the analysis by attempting to analyse only the sorbate. The potential losses can be estimated in dedicated experiments.

The report describes the progress during the first year for each participant. CEA has received one sample out of 5 and will obtain the others shortly after. CEA-LARC has tested combustion and total recovery of C-14 as CO_2 in soda water to obtain 100% yield. For organic-inorganic fractions, a lower yield is obtained for the organic part, which probably needs further improvement. CEA-LRMO aims to analyse the size and families present in the samples. ENEA and FZJ report development of various analytical methods for C-14 analysis.

State of the art report: The effect of gamma-radiolysis during storage is discussed. FZJ is concerned about gamma dose (Co-60) in the samples. In general, analytical methods are discussed in this state of the art report; the separation of organic/inorganic fractions much less and a short section on degradation (radiolytic or chemical for SIER) is presented. An exhaustive and alphabetical reference list, including all cited papers is included.

4.6.4 D5.2 WP5 Graphite Annual Report – Year 1

A large number of participants had a task to review the data obtained in the Carbowaste EU-project. The report starts with a concise executive summary and summarises once more the work described by all participants at the end of the report. INPL has studied migration of implanted C-13 as a surrogate for C-14 and migration of implanted N-14. Annealing up to 1600 C shows no migration of C-13. Irradiation with He showed surface corrosion when the beam was stopped at the surface, while no migration was observed in the other cases. Julich has already some results and their accelerated leach tests, as well as their data on C-14 release in humid air seem interesting. LEI has accomplished the review of Carbowaste and calculations of RBMK graphite activation will be compared with sample analysis from Ignalina. IFIN-HH presents good preparations, an AMS device with Cs-ion sputtering and a method to analyze total inventory. This is an impressive effort if one considers the relatively limited amount of graphite to be disposed.

RWM presents a thorough and reasonable interpretation of experimental data from graphite leaching under various conditions in the last part of the report. A potential mechanism for the release of organic compounds in the gas phase during water leaching would be appreciated.

4.7 *Andra Review Comments*

4.7.1 D1.4 – CAST 2nd GAM Minutes

It would be interesting to highlight the main risks linked to the Risk Management Plan. Another idea would be to put forward the common topics (and sometimes the common work) between the different WPs like the analytical techniques to characterize carbon-14 speciation.

4.7.2 D3.5 WP3 Zircaloy Annual Report – Year 1

About 55,000 CSD-C will be disposed of in the French deep geological disposal (Cigéo). Carbon-14 inventory is mainly located in zirconium alloy (Zircaloy 4, M5 and Zirlo). That is why there is a clear need to have a better understanding of the inventory and the source term of carbon 14 from zirconium alloys. According to the French R&D program, the main issues are the following:

- Inventory and localization:
    - What is the Carbon-14 activity depending on the nitrogen content and the burnup? Are there any discrepancies between measurement and calculations?
    - What is the Carbon-14 inventory in the zirconia layer?
    - What is the concentration profile of Carbon-14 inside the hull?
- Source term
    - What is the corrosion rate of zirconium alloys under anoxic conditions in cementitious environment at low temperature (less than 50 °C)? Do the following factors have a potential effect on the corrosion rate: hydrides, galvanic coupling, radiolysis?
    - What is the dissolution rate of zirconia under the same conditions taking into account the influence of complexing species and its history in reactor?
    - What is the speciation of released Carbon-14?

The main issue is the speciation of Carbon-14 because organic compounds need to be identified in order to use a specific Kd in the safety assessment.

According to table 11, WP3 covers the main issues regarding Carbon-14 inventory and source term. Most of the experiments are dealing with the main issue (C-14 speciation).

Concerning Carbon-14 inventory, RWMC and KIT will carry out calculations/measurements to evaluate the carbon-14 activity both, in the metal and in zirconia. It will also be interesting to do measurements and calculations for the same samples in order to evaluate the assumptions and the input data used for calculations.[2] It seems that this program will not give more information concerning the Carbon-14 profile (Is it safe to assume a uniform distribution of Carbon-14, that is to say congruency between Carbon14 released and zirconium alloy corrosion and / or zirconia dissolution).

Concerning carbon-14 source term, the R&D program addresses the corrosion rate of zirconium alloys and the speciation of Carbon-14 released. It is foreseen to use different techniques to measure the corrosion rate of zirconium in alkaline media at room temperature. The sensitivity of the different techniques will be assessed and only the relevant ones will be considered: gravimetric measurement[3], H_2 measurement, ^{14}C measurement, Linear Polarization Resistance (LPR)[4]. According to D3.1, hydrogen measurement techniques lead to an underestimation of the corrosion rate due to the significant hydrogen pick-up ratio of zirconium alloy estimated at 90%. Most experimental conditions are relevant regarding repository conditions: cementitious water (NaOH or $Ca(OH)_2$), anoxic conditions, low temperature…Some experiments will be carried out in acidic conditions, which is a way to assess C-14 inventory, but the question of the representativeness of the C-14 organic compounds is not detailed. At the present stage it is not sure whether LSC techniques will be accurate enough to assess Carbon-14 speciation. Therefore, accelerated mass spectrometry (AMS) is also envisaged. The consequences on the WP3 planning are not clearly identified[5].

4.7.3 D4.2 WP4 Ion-Exchange Resins Annual Report – Year 1

IERs are widely used in EDF nuclear facilities for the purification of water coolant. Important applications include primary circuit, secondary circuit and effluent treatment. The SIERs are then conditioned onsite by encapsulating them in an epoxy matrix. SIERs are

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[2] This point was discussed during the joint WP2&3 meeting on 28-29 May 2015. Nagra offered the possibility of doing calculations.

[3] I have no confidence in the likely effectiveness of such measurement but it seems that it has now been discounted as a possible technique.

[4] A new technique was added in the last joint WP2-WP3 meeting: Co-60 measurements.

[5] It seems that this point was discussed at the last meeting

mainly an issue for surface repositories due to their organic carbon-14 inventory. The main issues are to determine carbon-14 speciation in the SIERs and to evaluate the variability of the speciation depending on the operating conditions.

The following studies should shed some light on these issues:

- The studies carried out by CEA are expected to provide the carbon-14 speciation in PWR SIERs and also a characterization of carbon-14 organic compounds. The first results on virgin IERs are encouraging (complete or near complete recovery of carbon-14). The analytical strategy is clearly detailed and is based on previous studies on different waste.

- ENEA studies focus on bibliographic research but also on carbon-14 inventory in PWR SIERs and on carbon-14 speciation (ratio between organic and inorganic carbon-14).

- SKB results are interesting because they deal with both PWR and BWR reactor, and they show that carbon-14 accumulation is a function of the operational conditions of the reactor. SKB assume that organic carbon-14 species are most likely simple organic acids but there are no bibliographical references.

FZJ studies focus on BWR SIERs and it is unlikely that the results may be extrapolated to PWR SIERs. It is the same problem with INR studies on storage tank SIERs.

Previous studies on polymers have shown that identified organic compounds represent a small fraction of the TOC. From a safety assessment point of view, it would be useful to assess this ratio for SIERs.

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