EUROPEAN COMMISSION

European Research Area

CArbon-14 Source Term

CAST

Advisory Group Review of Year 2 WP Annual Reports and Minutes of Third CAST GAM (D1.7)

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Date of issue of this report: 18/04/17

The project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 604779, the CAST project.		
Dissemination Level		
PU	Public	**X**
RE	Restricted to the partners of the CAST project	
CO	Confidential, only for specific distribution list defined on this document	

CAST – Project Overview

The CAST project (CArbon-14 Source Term) aims to develop understanding of the potential release mechanisms of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal to underground geological disposal facilities. The project focuses on the release of carbon-14 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

CAST		
Work Package: 1	CAST Document no. :	Document type:
Task: 1.1	CAST-2015-D1.7	O = other
Issued by: RWM		Document status:
Internal no.: not applicable		Final

Document title
Advisory Group Review of Year 2 WP Annual Reports and Minutes of Third CAST GAM (D1.7)

Executive Summary

One of the tasks of the CAST Advisory Group is to review progress towards meeting the various project goals. This report represents the third formal review performed by the Advisory Group and considers material published in the minutes of the third CAST General Assembly Meeting and the Year 2 annual progress reports from Work Packages 2, 3, 4, and 5.

Whilst the first year of the CAST project was one of reviewing the current state of knowledge, establishing experimental protocols and obtaining irradiated samples, the second year was focussed on obtaining new data and information.

Progress continues to be made in all Work Package areas, with a number of organizations commissioning corrosion/leaching equipment and starting exposure tests.

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1 Introduction

One of the tasks of the CAST Advisory Group is to review progress towards meeting the various project goals. This report represents the third formal review performed by the Advisory Group and considers material published in the minutes of the third CAST General Assembly Meeting (Williams and Scourse 2016) and the Year 2 annual progress reports from Work Packages(WP) 2, 3, 4, and 5 (Mibus et al. 2015, Necib et al. 2015, Bucur et al. 2015, Toulhoat et al. 2015).

As previously, progress in each of the four work packages is presented in terms of the contributions to three key areas in the development of a ^{14}C source term, namely:

- Inventory - where, how much, and in what form is the ^{14}C present in the waste form?
- Release - what is the rate and mechanism of ^{14}C release, including the speciation?
- Transport/reaction - once released, does the ^{14}C subsequently react in the near-field and how is it transported?

Information is required in each of these areas for the four different waste forms (steels, Zircaloys, spent ion-exchange resins (SIER), and irradiated graphite) in order to develop a robust source-term expression.[1]

C-14 production takes place in the atmosphere [Libby, 1946] where thermal neutrons, which are secondary particles of cosmic rays interaction in the atmosphere, react with N-14 to create ca. 2 atoms of C-14 atoms /cm^2 sec (see Fig 1). This naturally occurring, cosmogenic C-14 is quickly oxidized and enters the global carbon cycle. The addition of anthropogenic C-14 takes place due to 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 C-14 show that the anthropogenic pool is dominated by the atmospheric nuclear tests that took mostly place between 1954 and 1964 AD [Yim, 2006]. Monitoring of

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[1] Although information on the transport and reaction of ^{14}C is pertinent to WP6 on PA issues, the CAST participants and coordinators broadly agree that consideration of reactions involving ^{14}C away from the waste form are out-of-scope of the experimental WPs.

operating nuclear power plants (NPP) allows the estimates of local C-14 releases mostly as $^{14}CO_2$ and other gaseous forms [LEVIN ET AL., 1988, HUA ET AL., 2013].

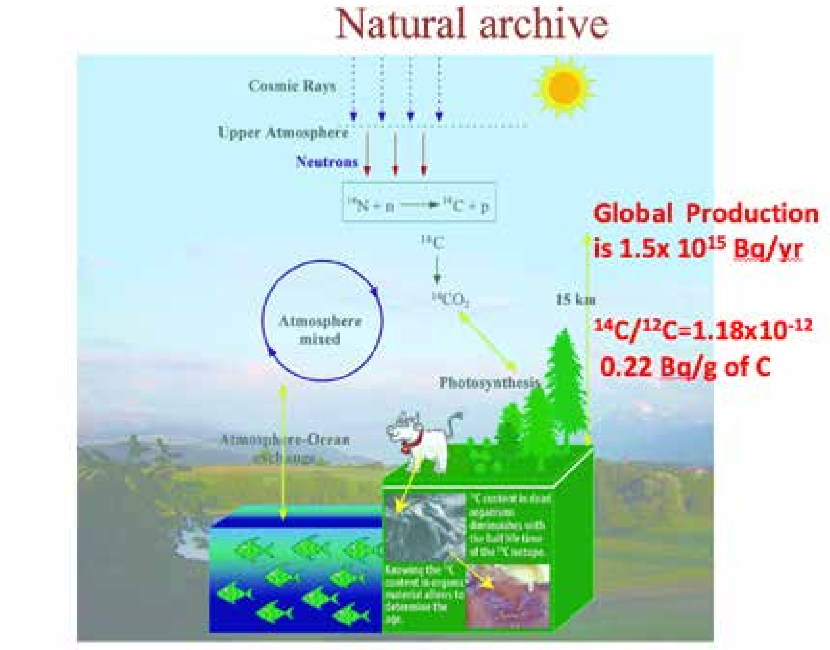


Fig 1. Radiocarbon in nature—production and distribution (modified from [HAJDAS, 2008])

The C-14 releases during long-term management of radioactive waste have to be estimated. The reports of the 2nd year activities of WPs in the CAST project summarize the analytical development and tests that were performed prior to quantification of organic and inorganic C-14 releases under simulated disposal conditions.

2 Review of 2015 GAM Minutes and Year 2 Work Package Annual Reports by Fraser King

2.1 *Minutes of CAST General Assembly Meeting 3*

The third CAST General Assembly Meeting was held in Bucharest on 14-15 October 2015 (Williams and Scourse 2016) and was preceded by a day of meetings for the different work packages. The meeting minutes (Williams and Scourse 2016) represent an accurate description of the presentations and discussion that took place during the GAM.

Various specific comments relating to different WP that arose from the review of the GAM minutes include:

- Of the various experimental WP (WP 2-5), those concerned with steels (WP2) and Zr alloys (WP3) are perhaps least well-advanced in terms of understanding the chemical characteristics and distribution of ^{14}C. Factors such as the distribution between the base metal and the oxide or the precise chemical nature of the ^{14}C remain uncertain, but could have important implications for the rate of release. In this regard, there seems to be a better level of understanding for SIERs (WP4) and i-graphite (WP5).
- In the absence of other information, it may be necessary to continue to assume congruent release of ^{14}C for steels and Zr alloys. That being the case, it will be important to develop recommended (distributions of) corrosion rates for use by PA. It is noted that there is significant variability in the corrosion rates reported to date, especially for Zr alloys, resulting from different specimen histories, exposure times, and, especially, different experimental techniques.
- Although it is generally agreed by participants that consideration of the transport and reaction of ^{14}C lies outside of the scope of CAST, the potential importance of microbial processes in determining the speciation and transport of ^{14}C should at least be acknowledged in future documentation from WP6.

2.2 *WP 2 Steels - Annual Report*

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

- Task 2.2: Development of analytical methods for measuring ^{14}C speciation
- Task 2.3: Corrosion experiments and measurements of released ^{14}C

The areas in which the 2015 activities have contributed to an improved understanding of the overall ^{14}C source term for steels are highlighted in Figure 2 and are described in more detail below.

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

This task appears to be well in hand, with several participants having developed techniques for sampling, determining the speciation, and analysing gaseous and liquid samples. Not all labs are analysing both liquid and gas samples, and the extent to which the speciation of the samples will be determined also varies among the participants. Some labs appear to be focussing on the measurement of organic C and there is some evidence to support this focus for steel samples. A limited number of participants will have access to the more-sensitive AMS method for quantifying the amount of ^{14}C released. Those labs relying on LSC may have difficulty in quantifying small amounts of ^{14}C from short exposure periods, thus limiting the ability to resolve the time-dependence of the ^{14}C release.

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

Much of the effort by the various participants in 2015 was focussed on commissioning experiments to determine the ^{14}C release rate as a result of corrosion of stainless or carbon steel. Of the 11 participants reporting, nine either started experiments or had well-developed plans. There was clear progress from the previous year, especially with obtaining activated samples.

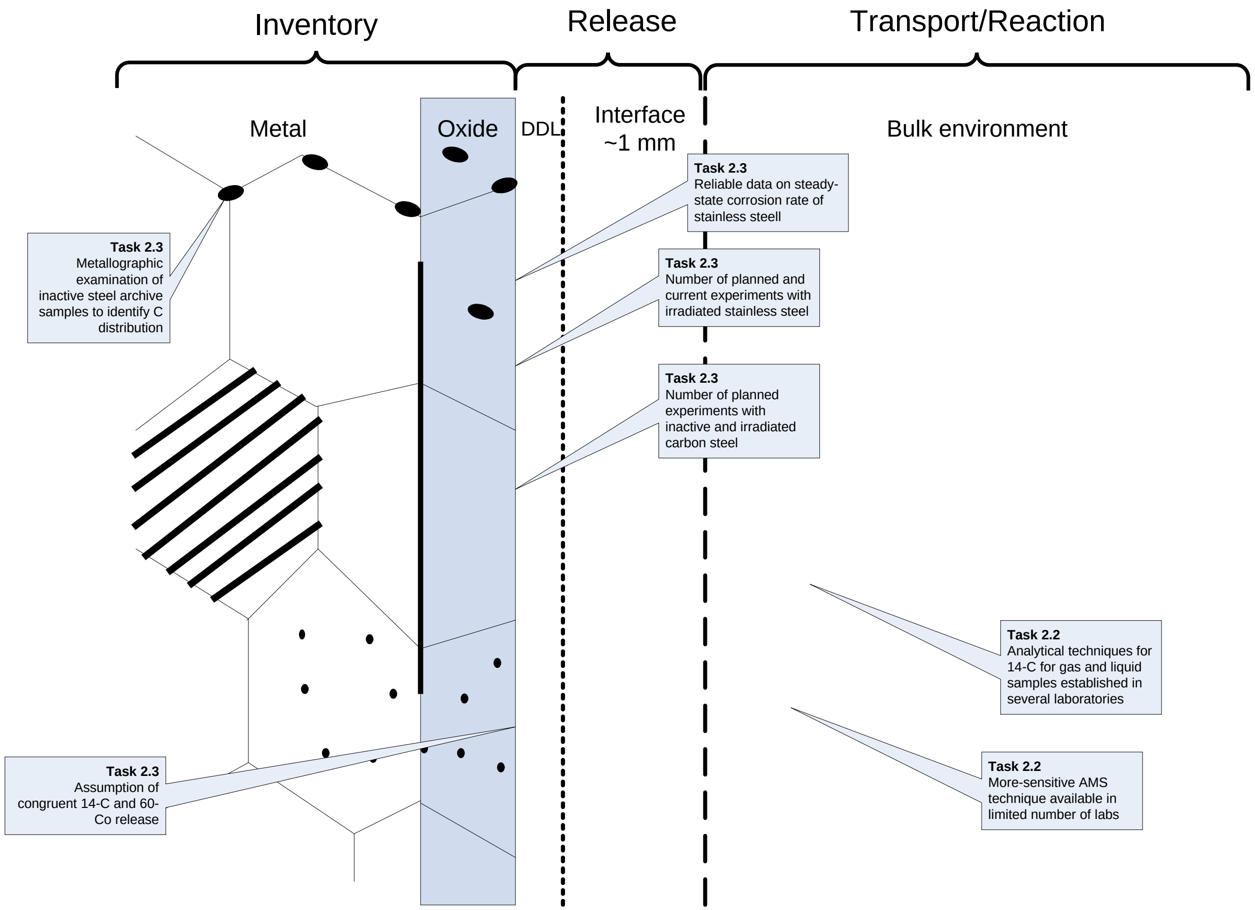


Figure 2: Summary of Progress in Developing a ^{14}C Source Term for Steels in 2015.

The following observations are based on the review of the Year 2 progress report:

- There is relatively little discussion of the characterization of the corrosion samples, although SCK-CEN report the results of metallographic examination of inactive carbon steel archive samples and have plans for examining the corresponding activated samples. Metallographic examination, especially of activated samples, may provide evidence for the chemical nature and distribution of the ^{14}C.
- Few of the participants report attempts to measure corrosion rates. Measurement of the corrosion rate is important if the assumption of congruent release of ^{14}C is to be used for PA. One participant is measuring ^{60}Co, as well as ^{14}C, presumably to use the release of the former as a measure of the corrosion rate of activated (stainless) steel. It is not intuitively obvious that Co should be released congruently with corrosion of stainless steel; indeed, the evidence presented suggests that 0.14% of the Co was released during leaching with only minimal oxidation of the sample. It is recommended that more effort be put into measuring corrosion rates to determine whether the assumption of congruent ^{14}C release is valid.
- A number of participants are calculating the inventory of ^{14}C based on different activation codes. This is useful if the initial $^{14}N/^{17}O$ content is known, but is of limited use if only the specified contents are available.
- Because of the difficulties associated with commissioning active experiments and obtaining activated samples, it is likely that the exposure period of the corrosion experiments will be less than the target of 12 months for many of the participants.
- Given the relatively short exposure periods and the expected low corrosion rates, it may be difficult to resolve short-term from long-term ^{14}C release rates.
- There is more effort on stainless steels (six participants) than on carbon steel (one participant), with one participant planning on studying both materials. Does this emphasis on stainless steels reflect the proportion of these alloys in ^{14}C waste streams?
- Ultimately, the results from the various experimental studies will be synthesized (Task 2.4). Will this synthesis simply be a collation of the different pieces of work, or will there be a critical review of the different studies with recommended values of

corrosion rates, ^{14}C release rates, ^{14}C speciation and distribution between gaseous and dissolved forms, etc.?

2.3 *WP 3 Zircaloy – Annual Report*

The WP3 annual report describes progress made in 2015 on two tasks (Necib et al. 2015):

- 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 annual report contains a number of useful tables that summarise the contributions of each participant to the various tasks. These tables summarize the irradiated and unirradiated samples being tested, the analytical techniques to be used or under development, the leaching conditions for both irradiated and unirradiated samples, and the techniques and existing data on corrosion rates.

The areas in which the 2015 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.

2.3.1 Task 3.2: Development of analytical techniques

The work on developing analytical techniques for ^{14}C has been coordinated with the similar task in WP2 as many of the techniques to be used are the same. As reported above in Section 2.2.1, the development of these analytical techniques seems to be well-advanced. It will be interesting to see whether the techniques are sufficiently sensitive to quantify and determine the speciation of the small amounts of ^{14}C expected to be released from the corrosion experiments.

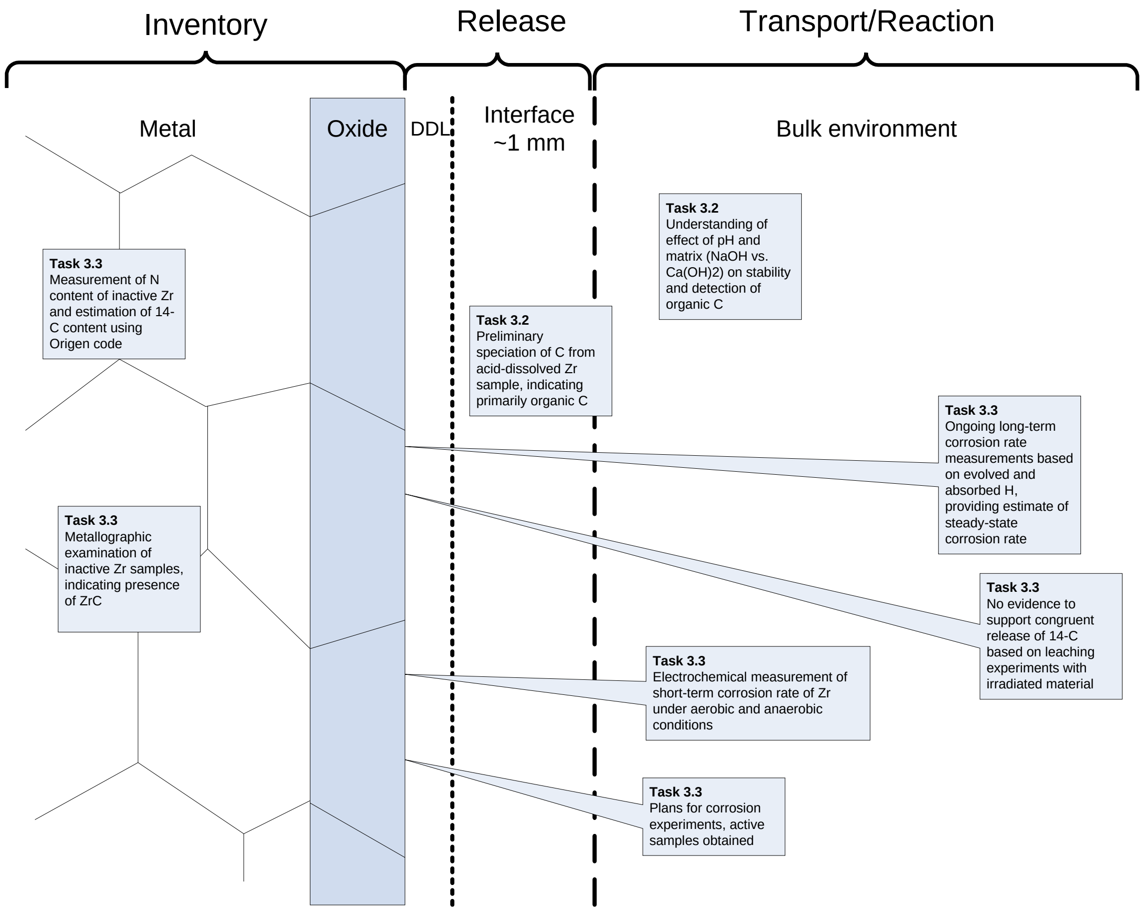


Figure 3: Summary of Progress in Developing a ^{14}C Source Term for Zircaloy Cladding in 2015.

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

It has been challenging to obtain irradiated Zr samples for corrosion testing and many of the participants were in the process of planning and commissioning experiments during 2015.

In looking forward to the point at which data become available, an important current uncertainty is whether ^{14}C is released congruently (with corrosion of the matrix) and whether there is an IRF (perhaps representing the ^{14}C contained in the oxide). Four of the participants plan to determine corrosion rates as part of their studies. Of these groups, two are using, or plan to use, electrochemical techniques in short-term experiments. The application of electrochemical techniques is challenging for passive materials, such as Zr, where there can be substantial voltage drop across the surface oxide. In addition, electrochemical tests are inevitably short term, and it is apparent from the RWMC data that the corrosion rate of Zr alloys continues to decreases over a period of several years before achieving an apparent steady-state value. The best estimate of the long-term corrosion rate currently available comes from the work of RWMC.

A number of the groups will monitor corrosion by measuring the time-dependent release of ^{60}Co. The validity of this measurement should be demonstrated by comparing the ^{60}Co release rate with reliable measurements of the corrosion rate. Data presented by RWMC suggests that different radionuclides are not released congruently.

As with the work on steels in WP2, a limited amount of material characterization is planned, or has been completed. A more-thorough understanding of the chemical nature and distribution of ^{14}C in the irradiated material would be helpful.

2.4 *WP 4 Ion-exchange Resins – Annual Report*

Of the four tasks in WP4, those for which progress was reported in the annual report (Reiller et al. 2015) were:

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

There are a number of challenges in developing a source term for ^{14}C release from SIERs for use in PA, including:

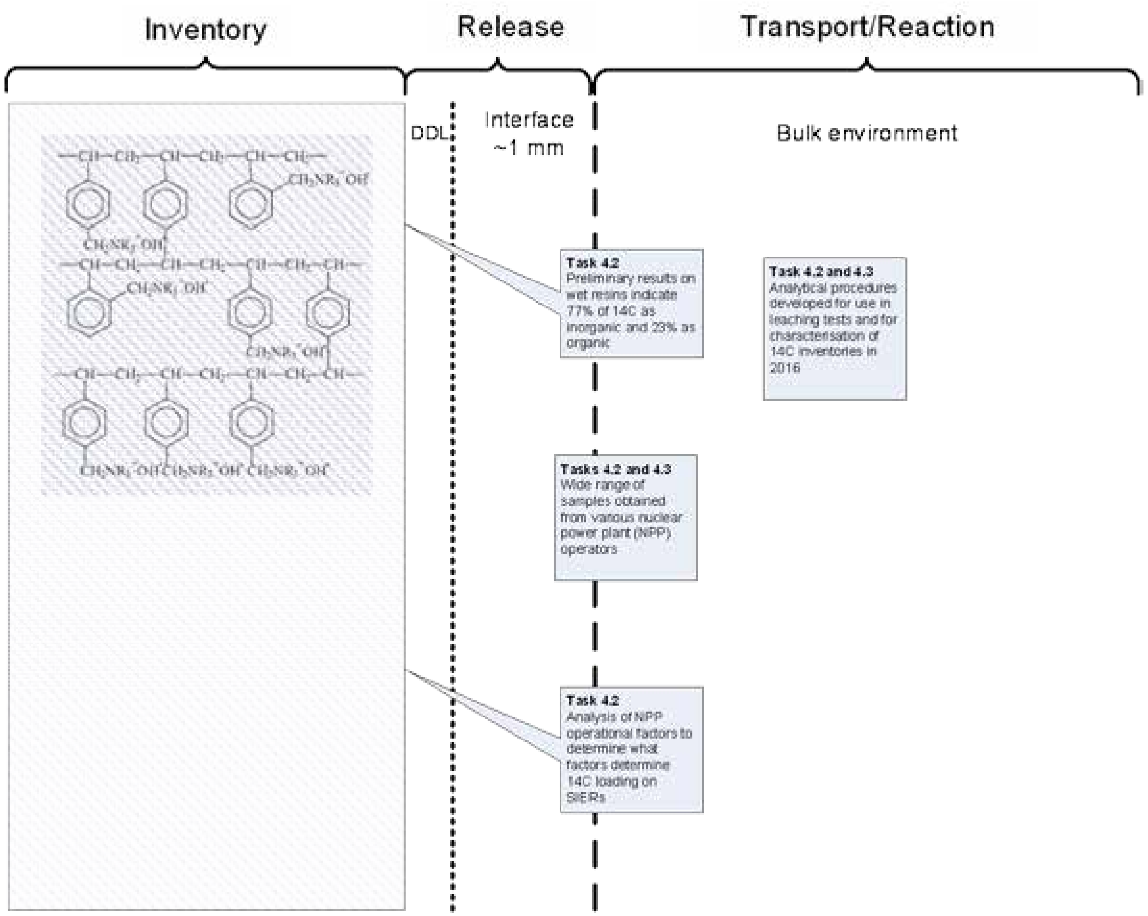
- There is a wide range of SIER types and locations within the reactor operating circuits.
- ^{14}C may be lost in the gaseous form during storage, complicating the estimation of the inventory.
- SIERs may age due to gamma irradiation damage, thus potentially affecting the release rate and mechanism.
- SIERs may be grouted with cementitious material, the impact of which will need to be accounted for.

The areas in which the 2015 activities have contributed to an improved understanding of the ^{14}C source term for SIER are highlighted in Figure 4.

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

All participants were in possession of SIER samples during the reporting year.

The planning and development of analytical procedures for characterising the ^{14}C content of the samples continued during the year. Preliminary data from CEA suggests that, at least in the samples obtained, the majority of the ^{14}C (77%) is present as inorganic C and a minority as organic.



Task 4.2
Preliminary results on wet resins indicate 77% of 14C as inorganic and 23% as organic

Task 4.2 and 4.3
Analytical procedures developed for use in leaching tests and for characterisation of 14C inventories in 2016

Tasks 4.2 and 4.3
Wide range of samples obtained from various nuclear power plant (NPP) operators

Task 4.2
Analysis of NPP operational factors to determine what factors determine 14C loading on SIERs

Figure 4: Summary of Progress in Developing a ^{14}C Source Term for Spent Ion-exchange Resins in 2015.

Given the variability in the types of SIERs, SKB started an analysis to try to correlate plant operational factors with the inventory and speciation of ^{14}C.

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

Various operational and licensing issues delayed testing for many of the participants in 2015. Progress is expected in 2016 since experimental protocols and samples are now in place.

2.5 *WP 5 Graphite – Annual Report*

Of the five tasks in WP 5, those for which progress was reported in the annual report (Toulhoat et al. 2015) were:

- 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
- Task 5.4: New waste forms and ^{14}C decontamination techniques for i-graphite

Compared with the other waste forms (steels, Zr, and SIERs), the current level of understanding of the nature and properties of ^{14}C in i-graphite appears to be more advanced, presumably as a result of information from prior related projects on ^{14}C wastes. As a result, participants in WP5 are addressing more-fundamental issues than in the other WP, such as:

- What is the spatial distribution of ^{14}C in i-graphite?
- Can we pre-condition (or decontaminate) the waste to improve the performance under repository conditions?

The areas in which the 2015 activities have contributed to an improved understanding of the ^{14}C source term for i-graphite are highlighted in Figure 5.

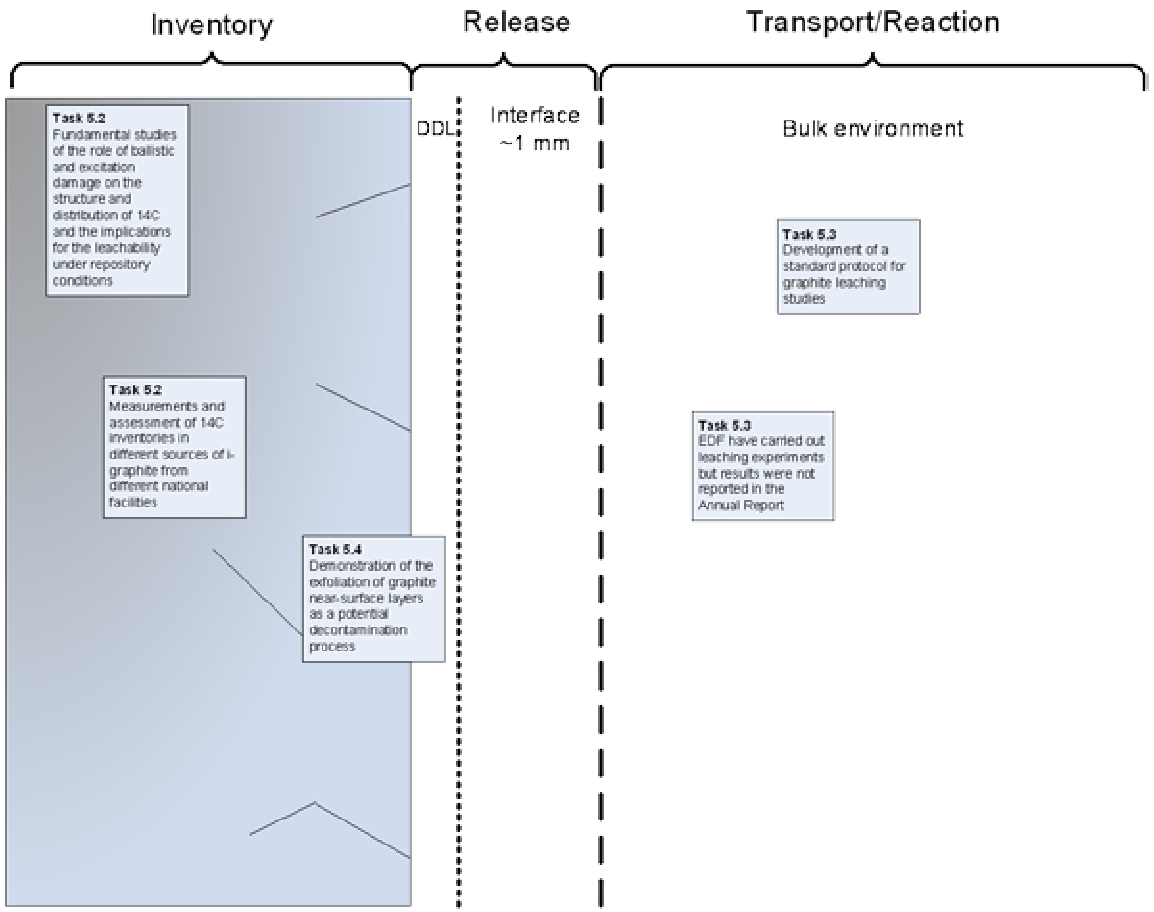


Figure 5: Summary of Progress in Developing a ^{14}C Source Term for Irradiated Graphite in 2015.

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

An example of the more-fundamental work being carried out in WP5 are the studies by IPNL on the effect of irradiation and temperature on the distribution of implanted ^{13}C and the associated bonding. This work highlights the damage caused by irradiation, but the reordering tendency of elevated temperature. The results of this work may also have practical implications for the release of ^{14}C under repository condition.

This fundamental work is complemented by efforts by other participants to characterise the inventories of both i-graphite and of ^{14}C from various decommissioned reactors.

2.5.2 Measurement of release of ^{14}C

A standard protocol for leaching tests for use by the different participants was developed during 2015, but no results were presented in the annual report. The majority of participants have obtained i-graphite and many have prepared samples in preparation for leaching in Year 3.

2.5.3 ^{14}C decontamination techniques for i-graphite

Because of the near-surface distribution of ^{14}C in i-graphite, there is the possibility of decontaminating the waste or at least of removing part of the inventory associated with the surface layers. ENEA have developed an exfoliation technique based on sonication in organic solvents.

3 Review of Year 2 Work Package Annual Reports and 2015 GAM Minutes by Irka Hajdas

The annual report of the 2nd year of activities of Work Packages 2,3,4 and 5 are reviewed with focus on planned C-14 content analysis and analytical approach.

3.1 *WP2 Steels (2nd year report)*

Annual report of the 2nd year of activities of Work Package 2

In Task 2.2 and 2.3 techniques for measurements of C-14 content in products of leaching (liquid or gas) is of main concern. Collaboration of PSI and Armines (WP3) to establish protocols for identification of released molecules and their C-14 content is focusing on application of the AMS technique. PSI is developing an interface that would allow a direct input of CO_2 from the HPLC & GC to the AMS (Uni BERN).

Twelve organizations participate in WP2

1. Amec Foster Wheeler, (former AMEC, UK) in collaboration with RCD—equipment for selective capture of volatile molecules of C-14 from the gas phase and C-14 analysis. Experiment of leaching planned in a hot cell (joint work with NRG) and direct transfer of gas containing C-14 into new system.
    a. 3 Soda lime columns for trapping the CO_2, CO and CH_4 (after oxidation). The LSC background at 0.03 Bq.
    b. Tests performed on the mix of gases show high efficiency of trapping after each column (more than 95%). But this was on high carbon content gas. Expected low carbon content. However this was not tested yet.
    c. Blank experiment—results end of Dec 2015, not included in this report
2. Armines (FR)- speciation on C-14 formed in irradiated steels and Zircaloys and released when stored in cement-based repositories; studies of only liquid phase
    a. Carboxylic acids (long chains) formed during steel/iron corrosion formate, acetate, propanoate, butanoate, oxalate and malonate .

   b. Experiment workflow for liquid phase from leaching of irradiated material shown in Fig 3.1. Separation of organic molecules by ionic chromatography and is designed for LSC analysis of C-14. Carbon carrier will be added.
   c. Problem of radionuclides Co60, Ni59, Ni63, Fe55 and Sb125 passing the chromatographic separation and being collected with carbon, interference with LSC (here AMS would help)—here treatment in Chelex 100 resin
   d. LSC (Tri-Carb) for the present test on carboxylic acids spiked with few Bq of C-14 per fraction. For oxalate fraction 83% recovery was achieved.
   e. For corrosion products Quantulus type an ultra-low level counter will be used and mixing with scintillation cocktails will be optimized to achieve high sensitivity.
   f. No plans for AMS are reported

3. Ciemat, (ES) (here reported planning of experiments)
   a. Preparation of samples of activated steel from reactor and a question is how representative it is for the inventories of C-14?
   b. Leaching container designed, leaching experiment planned
   c. Speciation using GC/MS (gas) and IC (liquid)
   d. C-14 after GC/MS analyzed using LSC (Quantulus) as in 2d (Armines).
4. ENRESA (ES) properties of irradiated steel and activities of the cut piece (4352 g). The total initial C-14 activity: 7.72×10^{-2} MBq
   a. leachate released C-14 under detection limit of LSC (0.04-0.07 Bq/g)
   b. planned AMS analysis of the compounds, in collaboration with Ciemat and at AMS facility, Seville, Spain
5. JRC-ITU (EU)
   a. Stainless Steel cladding composition and Burn-Up – expected high C-14 content. Use of autoclave in the hot cell and a transfer (gas cell) of C to a glove box.
   b. Adoption of molecular sieve to trapping CO_2 after the irradiated cladding material is combusted. Tests planned for 2015/2016. Results important for comparison with modelled values of C-14 produced.
6. KIT (DE)

    a. modelling of C-14 production: main target for C-14 production are N14 and O17, these are not known, 500 ppm recommended by Sakuragi et al, 2013. The calculated value of 8.5x10^{5}Bq/g.
    b. Dissolution tests – H_2SO_4 as oxidant not suitable. Recovery tests using C-14 labeled sodium carbonate and sodium acetate, for inorganic and organic carbon, resulted in 99% and 95 %, respectively.

7. NRG (NL) dissolution experiments and equipment (pre-CAST)
    a. Chemical hot cell and RCD rig testing on irradiated and non-irradiated samples was planned for 2015,
8. PSI (CH) Design and first tests for GC-MS and IC separated carbon bearing compounds of corrosion products and their C-14 analysis using AMS technique
    a. released C-14 activity at the level of 0.64µBq, which is ca 3x activity of 1 µg of modern (natural) carbon. The dilution of 25 to 50% in the chromatographic path will reduce the activity, however the levels are still above the natural activities. The biggest challenge here is the mass of carbon required to feed the ion source. At least 10 µg of C is needed.
    b. Blank levels (0.02-0.06 F14C) were shown to be influenced by alkalinity 0.06F14C for Mili-Q water but 0.89 F14C for a solution of $Ca(OH)_2$. Keeping the samples at the neutral pH and freezing is to prevent the contamination with modern atmospheric carbon.
    c. No effect on blank values due to chromatographic separation
    d. Investigated dynamic range of AMS: 0.2 F14C to 50F14C high recovery but not 100 % for most samples of the samples, except 0.2 F14C. Sample 4.39 F14C (Figure 9.3) has poor recovery as well. An incorrect window set at chromatographic separation is mentioned as general cause for lower recovery. Needs more tests.
    e. The memory effect of AMS analysis were investigated and a factor for correction of this effect is shown to be effective. The effect is mentioned as to be in 'AMS machine' but was this investigated? It seems to me that this is a memory effect of EA i.e., a combustion step. Perhaps wet oxidation could be a good solution here [McIntyre *et al.*, 2016].

    f. Development of a direct GC interface for AMS analysis.

9. RWMC (JP) Estimates of Corrosion rates
10. SCK·CEN (BE) material for experiments: non-irradiated and irradiated carbon steel samples
    a. determination of nitrogen content: 19+/-0.4 (ppm)
    b. Activities of radionuclides: Co60 and Ru106 highest values based on gamma counting.
    c. Calculated C-14 based on nitrogen content 19 ppm, (60 to 175 Bq/g, first calculation and computer simulation respectively)
    d. TIC in leachates below detection limit of 5mg/L except for Blank NaOH (at the limit), TOC between 14.1 mg/L (blank _DW) and below detection limit of 5 mg/L for blank. Samples at 6.9-8.2 +/- 2.5 mg/L (DW and 0.032 M NaOH, respectively)
    e. Carboxylic acids detected in samples on the level of 0.4-0.36 mg/L (acetate), and 0.13-0.17 mg/L (formate), oxalate under detection limit of 0.05 mg/L
    f. LSC as a C-14 counting technique but AMS is planned

3.2 *WP3 Zircaloys (2nd year report)*

Annual report of the 2nd year of activities of Work Packages 3: devoted to development of analytical methods, characterisation of C-14 organic and inorganic molecules (Task 3.2). In Task 3.3. inventories of C-14 and release of C-14 from irradiated Zircaloy fuel claddings from different reactors BWRs and PWRs is investigated

1. Armines/Subatech, analytical development (Subatech) of speciation and detection of C-14 released from leached zircaloys. Detection using LSC and AMS(?)—this would be required if collecting compounds after HPLC
2. CEA: development of analytical procedures
    a. TIC/TOC after desalination 7/419mg C/L)
    b. Summary shown in the Table 5: Potential use of AMS (detection limit of AMS is 14C/12C =10^{-15} corresponding to 0.22x 10^{-3} mBq/mg of carbon, here 0.5 mBq/mL)

   c. ESI-MS for separation of carbon molecules, potential for C12/C13/C14 (has this been done previously?)
3. ITU/JRC procedures as described in the 2.2.5
4. KIT : “Description of Zircaloy-4 dissolution experiment in a shielded box”
   a. Irradiated samples #1-#6
   b. C-14 analysis using LSC: Inventory of Zyr-4 at ca. $3x10^4$ Bq/g for all types of irradiation
5. RATEN ICN (INR): Corrosion tests of un-irradiated Zy-4 samples, testing experimental set up for measurements of inventories of C-14 in irradiated Zy-4 from CANDU spent fuel
   a. LSC measurements following acid dissolution (diluted H_2SO_4/HF), oxidation and trapping of CO_2 in NaOH.
   b. Tests on un-irradiated Zy-4 spiked with C-14 for recovery, reproducibility and memory effect. No results presented in this report. Planning another washing solution for CO_2 implies not satisfactory results.
   c. Addition of an oven—oxidizing gaseous organic C-14, additional gas washing for inorganic species
6. RWMC Leaching and corrosion tests
   a. Irradiated Zy-2 claddings from BWR were analysed: part of sample was used for nuclides inventory and the rest for estimates of release of C-14 into gas phase after corrosion test.
   b. Corrosion rates estimates
   c. Thickness of oxide layer dependent of temperature
   d. Speciation of carbon using chromatography: need for AMS to quantify the C-14 content. Regulations in Japan’s AMS labs prohibit submission of samples. Another option is LSC.
   e. A design for direct MS analysis of gaseous carbon from leaching in a glass ampoule. Potential interface for AMS (?)
7. SCK/CEN Properties of Zircaloys, leaching and corrosion tests
   a. Metallography and Nitrogen content (ca. 17-25 ppm which is lower than in literature 40-80 ppm)

   b. Calculated C-14 content, first and computer simulated differ by factor 20 (1000 Bq/g and 20000 Bq/g for nitrogen content 25+/-2.6)—need to verify this.
   c. Results for leachates TIC/TOC as reported in WP2

8. In the Summary Table 15 shows C-14 inventories mostly calculated on the order 1-5 x 10^4 Bq/g; Table 16 summaries analytical development –for C-14 quantification LSC is the main method, with AMS being considered by 2 teams. Table 17 showing Current results on C-14 analyses (inventory + leaching in NaOH solution pH 12) shows the first result of quantification by KIT and RWMC. Significant differences are observed with low values (10^{-2} Bq/gr) by RWMC for Zr2 and high (up to 10^4) by KIT for Zr4. Is this a difference in material or this experimental conditions are so different?

3.3 *WP4 Ion-Exchange Resins (2nd year report)*

Annual report of the 2nd year of activities of Work Packages 4. Research of this working group focusing on of speciation, source term, leaching, and gaseous release of C-14 from spent ion exchange resins SIERs, was mainly dedicated to the development and implementation of analytical techniques

1. CEA-EDF – inventories of C-14 in SIERs from nuclear power plants (EDF-PWR reactors) and speciation of organic C-14
   a. Wide range of doses (different sampling location and storage history)
   b. C-14 recovery Tests on spiked IERs
   c. Irradiated wet samples were measured, reproduced total C-14 content of 5700+/-270 Bq/g (77% inorganic/23%organic)
   d. Measurements on dry resins show lower activities. Loss of C-14 on mineral form.
   e. TOC/TIC – significant portion in mineral form
   f. Ion Chromatography for detection and separation of carboxylic acids –plans of combining with LSC replaced by combined GC-MS. However this is not sufficient to quantify C-14.

   g. Proposal to use Electrospray Mass Spectrometry to separate 12C/13C/14C for molecules of molecular mass < 1000g/mol. Experiment planned with labelled palmitic acid

2. ENEA—planned analysis of 9 wet SIERs.
   a. Step combustion with CO_2 collected using carboxyl amine or alkaline medium.
   b. C-14 determined by LSC
   c. a system planned for separation of different fractions of carbon (compound specific)
   d. plans for Cavity Ring (SCAR C-14 analyser—Fig 10)
3. FZJ—forms of C-14 released from leached SIERs
   a. Samples chosen to: contain high levels of C-14, low gamma, different storage time, water and gaseous samples
   b. Focus on direct measurements and speciation
   c. Development as for i-graphites – exploring potential of separation using GC-MS, HPLC and LSC
4. INR: planned analysis of CANDU SIERs
   a. Total C-14 using LSC after combustion in oxygen flow (Sample Oxidizer)–testing for memory effect and recovery using C-14 labelled resins. The obtained results are encouraging 100% recovery, 0.04% memory effect
   b. Testes for inorganic C-14 measurements—acid stripping method for C-14 spiked resins. Recovery of C-14 at 90%, memory effect at 1%
5. SKB investigation of C-14 uptake on the IERs
6. ÚJV background activity of C-14 in different resins matrix estimated at 4 Bq/g

3.4 *WP5 Graphite (2nd year report)*

Understanding of factors that control release of C-14 from the stored irradiated graphite requires information of the C-14 inventories and distribution of C-14 in i-graphite, estimates of rate and speciation of C-14 released to solution and gas. In addition, waste treatment is investigated and its potential effect on C-14 release.

1. Investigation of C-14 by IPNL was dedicated to investigation of irradiation and temperature on migration of C-14. It appears that, in high temperatures, similar to

13C atoms also C-14 atoms will be stabilized in the matric of graphite. That might be important factor in the estimate of release.

    a. Inventories of C-14 in graphites from Ignalina show different levels of activities: for the inner part of rings C-14 activity was $2.6.10^5$ Bq/g, while for the outer part of rings it was $3.9.10^6$ Bq/g [Mazeika, 2010].
    b. Problems in assessment of Nitrogen content
    c. C-14 and 3H –common preparation for measurements LSC, 20 cpm above background
    d. Leaching test of TRIGA graphites planned to performed using protocol of 5.4 (by FZJ)

2. Work at ANDRA: estimates of release based on CARBOWASTE and speciation in leachates
    a. Very low content of C-14 in leachates—techniques to obtained higher concentrations
3. ENEA describes exfoliation process for graphites, but not yet on irradiated graphites. This is interesting future plan.
4. FZJ aimed at development of a common protocol for leaching. Also estimate of all the irradiated graphites in Germany. Disposal limits: $4x10^{14}$ Bq. Limits per container. Also dependent on storage conditions dry/wet. Cement uptake of CO2 – estimated at 40 yrs.
    a. Planned leaching experiments – graphite blocks with estimated activity of 10kBq/g, which was confirmed by measurements the 10 plates gave specific activity of $6x10^3$ to $1.2\ x10^4$ Bq/g (why this difference?) –
    b. Leachates: speciation HPLC-MS, LSC or AMS (?)
    c. Gas phase: LSC for inventory, C-14 speciation (GC-MS) but what is the activity measurement technique?
5. Contribution of IFIN-HH –measurements of C-14 inventories using AMS especially for distribution of C-14 in i-graphites. Specific activities (Table 2.8.2) estimate and does rate measurements. $3.4x10^4$ Bq/g (next to core) to $2.6x10^2$Bq/g (first graphite disc)

a. AMS technique described and analysis <u>planned</u> on 2 instruments: 9 MV for high levels of activity, 1 MV for low, natural levels:
b. Decomposition of graphite for LSC (combustion and NaOH trapping of CO2)

This overview of activities shows that most of the C-14 measurements are being performed by LSC. The results appear consistent. It would be helpful to have a summarizing table showing all the measured inventories from all the groups/experiments taking into account different irradiation time and other parameters.

3.5 *Review of the General Assembly Minutes GAM2*

WP2 Steels:

The report on a joined technical meeting of WP2 and WP3 (27-28 May 2015) PSI and a workshop on analytical methods on 29 May 2015 held at PSI was mainly dedicated to speciation of C-14 releases (gaseous and liquid). The low content of carbon requires AMS analysis. A goal of this development is chromatographic separation (IC and GC) coupled with AMS system. A procedure is being developed by PSI in collaboration with University of Bern.

Specification of N content in steels gives a maximum of allowed concentration leading to overestimation (by factor of 3 to 4) in calculation of C-14 content for irradiated steels. Also carbon content is overestimated.

Measurements of real nitrogen values on un-irradiated samples were offered by SCK.CEN which will help to obtain reliable C-14 values from activation calculations.

Corrosion Tests –instant release of C-14 in liquid and gas phases. LSC measurements are considered but potentially too low activities will require AMS.   Facility in Spain, Seville might be involved.

WP3 Zircaloys:

It has been reported that also for Zircaloys the N content (40-80 ppm) is overestimated leading to too high C-14 estimates. Specific activities of C-14: metal (80%) and oxide (20%).

Analytical development in collaboration with WP2: leaching / C-14 content of leachates (D3.2) is completed. Speciation following measurement after pyrolysis total C-14 release, and pyrolysis organic fraction remaining after acid treatment. Carbonate estimate by subtraction. Combined LSC-AMS approach i.e., for low carbon content AMS analysis will be applied. Established contact to Saclay AMS facility.

WP4 Ion-Exchange Resins:

At the technical meeting in Paris July 2015 leaching procedure using NaOH solution, pH 12.5, which would represent the conditions in cementitious deposit conditions. Reported by CEA when oxidation at 25 bar and sequential acid dissolution an agreement in C-14 content observed for wet samples but differences noted for dried samples. This is a subject to follow up.

New C-14 laboratory and step combustion system at ENEA. Also ENEA made first contacts and investigated potential for use of the new spectroscopic technique, named SCAR (Saturated-Cavity Absorption Ring Down Laser Spectrometry (GALLI et al., 2013) for C-14 analysis.

WP5 i-graphites:

Laboratory inter-comparison in estimation C-14 inventories difficult due to the different experimental conditions and acceptance criteria. In Task 5.3 FZJ and WG5 participants developed methodology that should unify the procedures, which is described in Report D5.4.

Analysis on TRIGA graphite (how long irradiation?) using LSC resulted in range of 4-9.5x10^3 Bq/g (0.2 g of powdered used). In connection to the standardization of procedures a standard reporting of C-14 content should be adopted by all working groups and institutes independent of the countries regulations.

Releases from graphites are dependent on location of C-14 i.e., effects of irradiation. It appears that most of C-14 is located in the grains and might be stabilized, which implies reduced leaching in deposits.

WP6 Safety Assessment:

Aspects of C-14 inventories, sources and transport in potential repository (clay, crystalline rock or salt disposal system) have been discussed. Significance of the CAST project in assessing potential dose increases as compared to natural background. Effect of microbial activities was considered and the potential input of $^{14}CH_4$ and $^{14}CO_2$. It is worth noting that only CO_2 should be considered as potential source of C-14 fixed into the plant tissues.

3.6 *Conclusions and recommendations*

From the C-14 analysis point of view a unified presentation of C-14 inventories is most important. 2nd year of CAST was dedicated to development of analytical methods, testing the special instrumentations. Most analysis of 14C content performed using the LSC technique. The planned applications of AMS technique has been tested by PSI (WP2). More development is ongoing. The plans to involve other (experiment or in development) techniques for 14C quantification are perhaps founded in the difficulties faced by research teams in finding the AMS laboratory to cooperate with (for example Japan). Presently some new AMS facilities are equipped with a gas ion source [WACKER *et al.*, 2013] as the facility in Bern. For example, facility in Debrecen (Hungary) has such ion source and experience in dealing with analysis on nuclear waste. Please see http://w3.atomki.hu/hekal/muszaki_hatter/ams_en.html or http://www.radiocarbon.org/Info/Labs.pdf for other laboratories around the world.

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