# CArbon-14 Source Term

# CAST

# General Assembly Meeting 3 Minutes (D1.6)

## 14 - 15 October 2015

## Bucharest

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## CAST – Project Overview

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

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

The objectives of the CAST project are to gain new scientific understanding of the rate of re-lease of carbon-14 from the corrosion of irradiated steels and Zircaloys and from the leaching of ion-exchange resins and irradiated graphites under geological disposal conditions, its speciation and how these relate to carbon-14 inventory and aqueous conditions. These results will be evaluated in the context of national safety assessments and disseminated to interested stakeholders. The new understanding should be of relevance to national safety assessment stakeholders and will also provide an opportunity for training for early career researchers.

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

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## Executive Summary

The third General Assembly Meeting for the CAST Project was held on 14th and 15th October 2015 in Bucharest. These minutes record the main points discussed at the meeting and are Deliverable 1.6 for the CAST Project.

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# 1 Introduction

## 1.1 *Welcome*

The meeting was opened by Steve Williams who welcomed everybody and noted that Ellie Scourse and Erika Neeft were unable to attend and had sent their apologies.

Christophe Davies noted that the first call under Horizon 2020 had resulted in the funding of the JOPRAD, SITEX-II, CEBAMA, MIND and Modern 2020 projects. These had all started in June 2015. There were also two parallel projects ANNETTE (Advanced Networking for Nuclear Education and training and transfer of expertise) and HONEST (History of Nuclear Energy and Society) – the latter probably not including geological disposal. The EC was moving towards joint programming in radioactive waste management and geological disposal involving WMOs via IGD-TP. The Second call for Horizon 2020 was launched on 14th October. Euratom may be extended to 2020 to align with EU funding process.

## 1.2 *Attendees*

| **Name** | **Organisation** |
|---|---|
| Mohamed Ali Bahri | Subatech / Armines |
| David Bottomley | JRC-ITU |
| Gunnar Buckau | EC-JRC |
| Manuel Capouet | Ondraf/Niras |
| Mauro Capone | ENEA |
| Miguel Cuňado | Enresa |
| Benjamin Cvetkovic | PSI |
| Christophe Davies | EC |
| Daniela Diaconu | RATEN ICN |
| Nikitas Diomidis | Nagra |
| Frank Druyts | SCK.CEN |
| Viorel Fugaru | IFIN-HH |
| Manuela Fulger | RATEN ICN |
| Dalia Grigaliuniene | LEI |
| Irka Hajdas | Independent Expert |
| Jaap Hart | NRG |
| Tiina Heikola | VTT |

| | |
|---|---|
| Viktor Jobbágy | SCK.CEN |
| Fraser King | Independent Expert |
| Solene Legand | CEA |
| Jose L Leganés | Enresa |
| Riccardo Levizzari | ENEA |
| Enrique Magro Lozano | Ciemat |
| Volker Metz | KIT |
| Jens Mibus | Nagra |
| Natalie Moncoffre | IPNL-CNRS |
| Sophia Necib | Andra |
| Simon Norris | RWM |
| Olli Nummi | Fortum |
| Christiam Postolache | IFIN-HH |
| Pascal Reiller | CEA |
| Corrado Rizzato | FZJ |
| Antonietta Rizzo | ENEA –check |
| Marina Rodriguez | Ciemat |
| André Rübel | GRS |
| Tomofumi Sakuragi | RWMC |
| Stéphan Schumacher | Andra |
| Natalia Shcherbina | FZJ |
| Steve Swanton | Amec Foster Wheeler |
| Nelly Toulhoat | IPNL-CNRS |
| Petr Vecèrnik | UJV Rez |
| Antonin Vokal | Surao |
| Steve Williams | RWM |

# 2 Update on Work Package 2 (Steels)

In Work Package 2 the D2.1 literature survey has been completed and published on the CAST website. The development of analytical development procedures has concluded and the resulting reports from PSI and Armines (D2.3 and D2.4) are in progress. The corrosion experiments are about to start. The Year 2 annual report from WP2 will be finalised in October.

A joint WP2 and WP3 technical meeting was held 27th and 28th May 2015 and followed by a workshop on analytical methods on 29th May 2015. One topic of discussion at the analytical workshop was provision of standard solutions for QA of solution analyses and to allow comparison of methods for stable carbon or carbon-14 (hereafter stated as '$^{14}$C') in solution. Any interested groups should contact Erich Wieland.

The major problem with $^{14}$C speciation analysis in the systems of relevance to CAST is the low concentration of $^{14}$C-containing species. This has resulted in the drive towards developing $^{14}$C Accelerator Mass Spectrometry ($^{14}$C-AMS) as a speciation method, by coupling with ion-chromatography (IC-$^{14}$C-AMS) for dissolved compounds and gas-chromatography (GC-$^{14}$C-AMS) for volatile compounds. This is being developed by PSI through collaboration with University of Bern and the development of techniques to oxidise $^{14}$C-compounds to $^{14}CO_2$ for $^{14}$C-determination. It is hoped that the combustion route for GC-$^{14}$C-AMS will be installed by end of October. The final goal is on-line separation and oxidation of hydrocarbons, alcohols and aldehydes, trapping these as $^{14}CO_2$ and transferring the trapped $^{14}$C to the $^{14}$C-AMS for analysis. The separation system means that other radionuclides are not present in the samples sent for $^{14}$C-AMS (the use of ion exchange to remove cations from solution samples is discussed in WP3).

The activation calculations in WP2 have been slightly delayed and LEI are now not able to contribute to this. The irradiation details will be distributed to those undertaking the activation calculations. However, the real nitrogen concentrations in the steels prior to irradiation are often not known. Manufacturers' specifications only usually give the maximum allowed nitrogen concentration. The use of such values in activation calculations gives rise to uncertainties in the calculated $^{14}$C inventories (often too high by a factor of 3 to 4). Measurements of real nitrogen values would lead to more reliable $^{14}$C values from activation calculations and SCK.CEN have offered to measure nitrogen in unirradiated samples.

The workshop discussed sample preparation prior to the corrosion experiments and agreed that there should be 'as little as possible' pre-treatment, rather than the use of standard pre-treatment methods. Corrosion rates would be monitored during the tests, e.g. by measuring $^{60}$Co and assuming this is released congruently during corrosion. The reliability of this assumption will depend on the number of measurements that can be made during the experiments. There is some evidence for an 'instant release fraction' from steels, which may be connected to release from oxide film. This may be an important contributor to the release of $^{14}C$ in the experiments but its importance can be judged by measuring $^{14}C$ releases with time.

The duration of the corrosion tests will be one year. Redox potentials will be measured. Two possible solutions may be used: either $Ca(OH)_2$ solution at pH 12.5 or NaOH solution at pH12.5, depending on the risk of $^{14}CO_2$ precipitation and the analysis methodology. Sodium hydroxide will have a higher background level of $^{14}C$ than calcium hydroxide. Analysis of solution and gas phases will be either by pre-concentration and liquid scintillation counting (LSC) or by $^{14}C$-AMS. LSC is not sensitive enough to determine speciation directly so AMS will be required. Quantitative detection limits need to be known in cases where concentrations of $^{14}C$ are not measurable. $^{14}C$-AMS may become available in Seville through a contact of Marina Rodriguez.

All but one of the test samples required for WP2 have now been obtained and all but two of the beneficiaries in WP2 have their C14 sampling arrangements in place already. The corrosion tests with activated samples are expected to start in the first half of 2016.

Some recent results include:

- RWMC have determined a corrosion rate of 0.4 nm $y^{-1}$ for stainless steel and found the amorphous oxide layer to be 3 to 4 nm thick;
- in tests with inactive steel PSI have found that the amount of organic material varies with method of manufacture and is released in first few days of an immersion test, mainly as formic and acetic acids;
- SCK.CEN also found that the main contribution to organic $^{14}C$ is likely to be acetic and formic acids;
- VTT have found that releases of inorganic carbon from stainless steel and iron carbide are below detection limit, only organic carbon.

# 3 Update on Work Package 3 (Zircaloys)

Task 3.1 is complete in Work Package 3 and the state of the art report (D3.1) has been published on the CAST website. The specification of nitrogen content for different types of cladding (PWR = Zircaloy-4, M5™ and Zirlo™, BWR= Zircaloy 2) is <80 ppm and generally 40 to 80 ppm. Zircaloy reacts with water to form an oxide:

$$Zr + 2\ H_2O = ZrO_2 + 4\ H_2$$

The oxide thickness depends on temperature and burn up. Some of the hydrogen is picked up by the zirconium and, for example, this can reach about 15% in a PWR. At low temperatures all the hydrogen forms hydride. The Zircaloy corrosion rate is affected by stability of the oxide layer and could be about 20 nm $y^{-1}$ in alkaline solution at room temperature.

In a similar manner to steels, most $^{14}C$ estimates from calculations are overestimates because of the use of the specification levels of nitrogen (40-80ppm). The specific activity of $^{14}C$ in the oxide is greater than in the metal, with about 80% of the $^{14}C$ in the metal and 20% in the oxide.

Analytical development in conjunction with WP2 under Task 3.2 is now complete. The focus in WP3 has been on leachate analyses and is being undertaken by CEA and Subatech. CEA are responsible for methods of analysis for distribution between organic and inorganic $^{14}C$, CEA and Subatech are responsible for methods for speciation of small carboxylic acids and CEA are responsible for speciation of other organic molecules:

- total $^{14}C$ - quantification by pyrolysis followed by LSC or $^{14}C$-AMS (about $10^3$ factor better detection than LSC);
- organic / inorganic $^{14}C$ distribution – acidification to remove $^{14}C$-carbonate followed by pyrolysis to determine $^{14}C$-organic. Inorganic 14C calculated by difference from total $^{14}C$;
- speciation studies (Fourier transform infrared (FTIR) for functional groups, IC for small carboxylic acids, GC-MS for low MW volatile organic molecules and

Electrospray–mass spectrometry (ESI-MS) for mw>100) require desalination and pre-concentration to prepare samples;

- the ability of ESI-MS to differentiate molecules of a carboxylic acid (palmitic acid) mono-labelled and uniformly labelled with $^{14}$C from the $^{12}$C equivalent has been demonstrated;
- the use of KCFC resin and Chelex 100 resin in combination to reduce total activity in solution (Cs and Co/Fe/Ni/Sr respectively) has been shown to remove at least 95% of the radioactivity in solution;
- the detection limit for $^{14}$C by Quantulus LSC for an individual sample is about 0.01Bq;
- contact has been made with AMS facility at Saclay.

Some recent results from the leaching and corrosion studies include:

- corrosion rates of unirradiated Zircaloy in RWMC studies have been shown to decrease with time over 2 to 4 years to between $10^{-3}$ to $10^{-2}$ µm $y^{-1}$ in pure water, sodium and calcium hydroxide solutions and in cement porewater, with the corrosion rate slightly lower in pure water;
- RATEN-ICN have measured corrosion rates of 3 to 480 nm $y^{-1}$ for unirradiated Zircaloy-4, oxidised samples (2.7 µm oxide film) have lower corrosion rates than ‘as received’ samples and the corrosion rate in aerated water is higher than in deaerated water for both;
- RWMC have found that some $^{14}$C might be incorporated in the oxide layer as release appears congruent with release of $^{60}$Co and $^{125}$Sb but not with the corrosion rate of the Zircaloy metal;
- dissolution of irradiated Zircaloy-4 in $H_2SO_4$/HF by KIT results in the release of $^{14}$C to gas and to solution, almost all the carbon-14 is released as organic compounds (with about 10% of this in solution and the rest as gas) and the total $^{14}$C agrees well with the calculated inventory (the next stage will be to investigate the effect of a hydrogen overpressure and then look at release under alkaline conditions).

The Year 2 annual report for WP2 has been drafted, but report D3.9 is delayed. A joint WP2 and WP3 meeting will be held in Madrid, hosted by CIEMAT, in May 2016.

From the results obtained to date the corrosion rate of Zircaloy would be around 1 nm $y^{-1}$ if it was estimated from the rate of $^{14}C$ release, but would be about 0.01 nm $y^{-1}$ based on the release of Zr to solution. This shows that understanding the release of $^{14}C$ requires further understanding of the role of the oxide film and the nature of the $^{14}C$ in this and the parent metal, and also on the effect of the hydride layer (which might give increased release rates).

# 4 Update on Work Package 4 (Spent Ion-exchange Resins)

It was confirmed that the spent ion-exchange resins (SIERs) samples necessary for the work programme of Work Package 4 have now been received.

SIERs from PWRs - EdF have supplied 5 samples to CEA, ENEA have SIER from Trino, SKB have numerous samples taken between 2009-2104 from Ringhals, UJV have SIER from Temelin (it is possible that UJV may acquire a further 2 samples but any work on these would be additional to their proposed scope of work under CAST) RATEN-ICN have received CANDU samples from Cernovoda.

SIERs from BWRs – FZJ have obtained 3 samples of BWR SIERs, SKB have numerous samples taken between 2009 -2013 from Forsmark and Oskarshamn.

A WP4 technical meeting was held on 4th and 5th June 2015 in Paris. At this meeting it was agreed that leaching in sodium hydroxide solution at pH 12.5 would be used to represent the high alkalinity of cementitious disposal conditions.

CEA have compared analysis by oxidation under oxygen at 25 bar or by sequential acidification and acid digestion (which also provides the inorganic (carbonate) and organic $^{14}C$ contents). Both methods gave the same result for the total $^{14}C$ content of a wet sample (and about three quarters of the $^{14}C$ was inorganic). However, there was a large discrepancy between the results from the two methods for a dried sample and this will be investigated further. The methodology for determining the speciation of $^{14}C$ in solution is being developed. Unfortunately, it has not proved possible to couple the existing liquid scintillation counting equipment to ion chromatography, so the use and qualification of ESI-MS is being investigated as described for WP3 above. Palmitic acid is being used as a model compound for this. Although this is a relatively high MW species it was thought possible that large molecules could be present in solution through scission of the polymer backbone and subsequent secondary reactions. Previous work by Hummel and Van Loon on the degradation of ion-exchange resins had been unable to identify all the degradation products in solution, showing the difficulty of analysing a real mixture of unknown degradation products.

FZJ have demonstrated the ability to separate anion exchange resin from cation exchange resins in mixed bed resin bead samples using vertical solution flow. The anionic resin rises towards the top of the column but the method cannot be used for powder samples. The degradation of ion-exchange resins under gamma irradiation is being studied. There was some discussion of how degradation might affect $^{14}$C release with the expectation that the bonds to the functional groups would break first (e.g. leading to the loss of amines from anion-exchange resins), with the backbone structure of cross-linked divinylbenzene being much more stable. Associated $^{14}$C could thus be released more rapidly as the material ages and could also be involved in secondary reactions.

ENEA closed their $^{14}$C laboratory in November 2014 and relocated this to a new facility that became operational in September 2015. There is new equipment for investigating $^{14}$C release at different stepped temperatures (950°C to 1200°C) with collection of the resulting $^{14}CO_2$. Samples of 10-year-old resin and new fresh material are being studied to determine whether the degradation seen in the 10 year old samples is because of storage or whether such degradation is present in original material. ENEA have been selected as a ‘beta-tester’ for a new instrument for $^{14}$C determination based on Cavity Ring Down Laser Spectrometry and will have the opportunity to apply this to the $CO_2$ fractions obtained from the ion exchange resins.

RATEN-ICN will determine the $^{14}$C inventory of SIERs from the Cernovada CANDU nuclear power plant, measure leaching of $^{14}$C under cementitious conditions and consider the effect of storage conditions. SIERs are stored under water in concrete vaults lined with epoxy at the power plant but no sampling or $^{14}C$ measurements on these resins has been undertaken. SIER samples for use in CAST were taken during maintenance of Unit 1. Total $^{14}C$ will be determined by destructive oxidation and the resulting $^{14}CO_2$ trapped with Carbo-Sorb and measured by liquid scintillation counting. Preliminary tests with Amberlite IRN-150 labelled with $^{14}C$ have shown a typical recovery around 97% and that memory effects from previous samples should not be a problem. Tests are ongoing to assess any potential interference from other radionuclides in spent resins. Inorganic/organic $^{14}C$ will be determined by acid dissolution and wet oxidation based on the method of Magnusson et al (2008) with measurement by LSC. The acid dissolution step has been trialled and refinement of the experimental design for this has increased the $^{14}C$ recovery from about 80% to 92%. The next step will be to complete the experimental design by adding the catalytic furnace to complete the $^{14}C$ trapping chain and trialling the wet oxidation step with labelled IRN-150, prior to determining the $^{14}C$ content of the Cernovoda SIERs.

# 5 Update on Work Package 5 (Graphite)

Progress on reports for Year 2 of WP5 is as follows:

- D5.4 Definition of the scientific scope of leaching experiments and definition of harmonised leaching parameters - in progress, draft available;
- D5.5 Review of current understanding of inventory and release of C14 from irradiated graphite - published;
- D5.6 Annual progress report, Year 2 - in progress, draft available;
- D5.7 Report on C14 distribution in irradiated graphite from the research reactor VVR-S using accelerator mass spectrometry and beta imaging – delayed because of issue with accessing samples.

It is often difficult to compare the results of different graphite leaching experiments because of different experimental conditions (often driven by different acceptance criteria or needs of national programmes). As part of Task 5.3 FZJ, in conjunction with other WP5 participants, have reviewed the range of leaching methodologies that have been used and developed a methodology for harmonized leaching conditions that may be used in CAST. This considers the following: vessel material; specimen geometry; temperature; leachant;

gas composition; sampling interval; test duration; leaching regime; and analyses and is described in the D5.4 report. Adoption of the recommendations should minimise the differences between experimental approaches and enable a more straight forward comparison of the results of $^{14}$C leaching experiments in different laboratories.

INR are undertaking studies on the measurement of release of $^{14}$C from graphite from the TRIGA research reactor. TRIGA was a double-core material testing reactor and the graphite arises from the thermal column of the steady state reactor (TRIGA SSR, 14 MW). The thermal column consists of 96 rectangular bricks of graphite (approximately 2.5t in total) encased in aluminium and placed in a stainless steel frame in the reactor pool. The graphite was imported in the 1950s from the UK. Attempts were made to determine the nitrogen content of unirradiated graphite samples by acid digestion but these were unsuccessful with no nitrogen detected and it is possible that gaseous nitrogen was lost prior to analysis. Total $^{14}$C measurements for the TRIGA graphite by combustion under oxygen and trapping of the resulting $^{14}CO_2$ for liquid scintillation counting have given results in the range $0.8 \times 10^3$ to $1.9 \times 10^3$ Bq for 0.2g powdered samples. Leaching experiments on 50 mm diameter cylindrical specimens in sodium hydroxide solution at approximately pH 13 under anaerobic conditions at 25 C are about to start. The inorganic/organic ratio of $^{14}$C in leachates from the TRIGA graphite will be determined by acid stripping followed by wet oxidation in a similar manner to the SIER leachates in WP4.

Understanding of the effects of neutron irradiation on $^{14}$C behaviour in graphite is being increased through studies by IPNL using $^{13}$C implanted HOPG (highly oriented pyrolytic graphite) as a simulant. In reactors, neutron irradiation causes atom displacement cascades leading to mainly ballistic damage and recoil carbon atoms transfer some energy through electronic excitation. Ion beam irradiation can be used to promote either ballistic damage or electronic excitation effects depending on the ion mass and its energy. Most of the $^{14}$C in irradiated graphite occurs in the grains and $^{13}$C is implanted at a depth of 200 to 400 nm in HOPG to simulate this. Samples are then ion irradiated under an inert atmosphere or coolant gas simulant at temperatures from room temperature up to 1000°C. Ballistic damage does not promote $^{13}$C release and irradiation at increased temperature leads to a re-ordering of the graphite and the $^{13}$C may be stabilised into new sp$^2$ bonding structures. In contrast electronic excitation does not promote $^{13}$C release, and shows very little reordering of the structure with increased temperature, and the $^{13}$C may be stabilised into sp$^{3}$ bonding structures. Thus, whatever the irradiation regime, $^{13}$C is not released and is stabilised into the graphite structure where increased temperature and irradiation have opposing effects leading to re-ordering and disordering respectively. This leads to the conclusion that $^{14}$C in the grain structure of irradiated graphite would be stabilised into new structures with increasing temperature. In the context of possible pre-treatment of irradiated graphite prior to disposal this implies that the stabilised $^{14}$C should be more difficult to remove but it also implies that leaching of $^{14}$C should be reduced under disposal conditions.

ENEA are investigating the ability of ultrasonic treatment in organic solvents to exfoliate and decontaminate irradiated graphite. Trials with HOPG and unirradiated nuclear graphite have shown that the exfoliation behaviours of both are similar and yields of 2 to16 wt% graphene are achieved. The formation of graphene indicates that the process has worked therefore $^{14}$C should be removed to some extent. The next steps are to apply the process to irradiated graphite from the Latina NPP and evaluate decontamination factors for $^{14}$C. Further optimisation can then be undertaken.

# 6 Update on Work Package 6 (Safety Assessment)

The first report fromWP6 titled ‘Handling of C-14 in current safety assessments - State of the art’ (D6.1) is under final review and should be published by the end of 2016. The next stage in WP6 is to contextualise the knowledge base against current safety assessment hypotheses to develop the D6.2 report. This considers:

- $^{14}$C inventories;
- $^{14}$C source terms; and
- the transport of $^{14}$C in clay, crystalline rock and salt disposal systems.

Tasks 2, 3, 4 and 5 of CAST will provide input to the first two of these three bullet points for steels, Zircaloys, SIERs and graphite. However, another source of $^{14}$C is irradiated spent fuel. Although this is outside the scope of the experimental work in CAST, irradiated uranium oxide can make the major contribution to the $^{14}$C inventory of a spent fuel rod from a light water reactor (LWR). Typically, 10 to 15% of the $^{14}$C in irradiated uranium oxide is treated as an instant release fraction (IRF) when water contacts the fuel after repository closure in safety assessments. In irradiated Zircaloys, the $^{14}$C in zirconia is considered to have an IRF (which may be all the $^{14}$C in the oxide and may be released as inorganic carbon) and the $^{14}$C in the metal cladding to be homogeneously distributed (which may be released as organic carbon). In assessing Zircaloy hulls arising from reprocessing of spent fuels the assumptions may include the absence of an IRF for $^{14}$C because of the acidic reprocessing treatment.

The $^{14}$C inventory in irradiated steels has been assumed to be homogeneously distributed as carbides that react with water on corrosion of the metal to form dissolved organic species or methane. Although no $^{14}$C IRF is usually assumed, in some cases a value of 10% has been used. Depending on their thickness, reactor internal components may be treated as a number of layers to take account of different activation levels at depth.

In many cases the $^{14}$C in spent ion-exchange resins has not yet been specifically considered in safety analyses. Carbon-14 could be released during storage and waste conditioning (e.g. during drying). Assumptions about a $^{14}$C IRF and speciation for SIERs differ but at least 25% is usually assumed to be inorganic and assumed release rates may be dependent on the waste packaging and its ageing.

In disposal systems in a clay host rock, diffusion combined with radioactive decay can be very effective in limiting the transport of dissolved $^{14}$C. The $^{14}$C speciation may have an important influence on the diffusion rate but, because of its relatively rapid decay compared to disposal timescales, even weak sorption can reduce the effective dose rate from $^{14}$C by one or more orders of magnitude. If isotopic exchange occurs between carbonate and calcite this could lead to efficient retardation of $^{14}$C. In contrast, the behaviour of organic $^{14}$C is not as well known. Methane is often conservatively assumed, which could with dissolve in porewater or migrate as a free gas mixed in a bulk carrier gas. Retardation is often conservatively neglected. Depending on the gas pressure and the properties of the host clay migration of a free gas phase could be through two-phase flow, pathway dilation or gas–induced fracturing (for more details see reports from the EC FORGE project). In a clay system $^{14}C$ is generally not a concern for HLW because of a containment period of at least several tens of thousands of years and the stability of the HLW matrix. Larger uncertainties exist in current assessments for ILW because containment time (if any is assumed) is much less than transport time and much more hydrogen gas could be formed. This leads to different scenarios of strongly-retarded diffusive transport and unretarded gas transport. However, $^{14}C$ may not be a primary determinant of safety in either case for a clay host rock.

In disposal systems in a crystalline host rock, the use of high integrity containers (e.g. copper) for spent fue1 means that $^{14}C$ will have decayed during the period of physical containment by the canister. However, $^{14}C$ can be an important contributor to dose from ILW in a crystalline rock where transport time along a fracture network may be short compared to the half-life of $^{14}C$ if uptake from solution is weak. For Zircaloy wastes an assumption of instantaneous release of $^{14}C$ from the oxide can have a non-negligible radiological impact.

In disposal systems in salt, a fill (e.g. such as salt grit) around waste containers will be compacted by the creep of the host rock leading to low permeability and porosity. Transport of dissolved $^{14}C$ would be by diffusion and very slow.

In concrete and cement-based engineered barrier systems small organic molecules are only weakly-sorbed, and may be affected by ageing (e.g. reduction of pH), although carbon dioxide is removed from solution through carbonation. Thus, there is considerable uncertainty in a safety assessment treatment of $^{14}C$ as dissolved organic molecules in a cement-based system.

Post-closure safety cases need to reflect an understanding of uncertainties. In the context of $^{14}C$ these include the inventory and distribution of $^{14}C$ in waste streams, the speciation of released $^{14}C$, rates of release from wastes including any rapid release (which may be treated as an IRF) and long-term corrosion behaviour of metals, retention factors (e.g. $K_d/R_d$) for organic compounds particularly in cement, stability of $^{14}C$ species in evolving repository conditions and during migration in the geosphere.

Some key themes that are emerging from WP6 are:

- the findings from CAST can provide qualitative arguments to support safety cases as well as quantitative data that feed into dose curve calculations;
- understanding of dissolved $^{14}C$ speciation will contribute to understanding potential retardation in cement and bentonite/clay systems;
- IRFs may have a non-negligible impact in some disposal concepts and the results from CAST may underpin or identify conservatisms in assumed values;
- a consistent understanding of $^{14}C$ inventories is important;
- it is important to consider how the experimental results relate to disposal conditions in different concepts and how they might be extrapolated over timescales of concern as conditions evolve.
- $^{14}C$ may be released from some wastes during waste packaging and conditioning and during interim storage - this may reduce the inventory of $^{14}C$ in some waste packages at the time of closure of a disposal facility.

INR presented an overview of the possible impact of microrganisms on $^{14}C$ speciation and migration. This covered the existence of microbial populations in deep geological environments, biochemical processes and potential effects on $^{14}C$ behaviour. An example of the inclusion of biogeochemical processes in modelling $^{14}C$ releases was given from the environmental safety case for the low-level waste repository (LLWR) in the UK. The conclusions of the overview were: $^{14}C$ can be subject to biogeochemical processes that can lead to changes in speciation and partitioning between solid, liquid and gas and depend on a number of factors; migration of radionuclides because of sorption of microorganisms seems to be negligible; oxidation of migrating of $^{14}CH_4$ to $^{14}CO_2$ in the surface environment leads to plant uptake of $^{14}C$.

There was some discussion on the ability of microbes to degrade organic polymers. It was noted that some polymers are quite resistant to microbial attack although additives leached from the polymer (e.g. plasticisers from polyvinylchloride) may be more susceptible. It may be necessary for other processes, such as chemical or radiolytic degradation, to break down the polymer structure to facilitate further degradation by microbial action. It is possible that complexing agents could be destroyed by microbes. In a cement system carbon dioxide will be trapped by carbonation of cement. Conditions may be more favourable for microbial activity in wastes during storage than in the high pH conditions associated with wastes grouted with cements. Microbes will tend to prefer the lighter isotopes of an element and thus some fractionation of isotopes occurs continuously in the natural environment. The impact of such effects for the isotopes of carbon are likely to be negligible compared to other uncertainties.

A WP6 technical meeting will be hosted by Nagra in Q1 or Q2 of 2016. This will focus on retention processes in clay, bentonite and cement but will include discussions on the preliminary integration of CAST results into safety cases. There will be an invited expert presentation on BIOPROTA. The D6.2 report should be completed in early 2016.

# 7 Update on Work Package 7 (Dissemination)

The first training course in CAST is organised by KIT on "C-14 behaviour under repository conditions" and is planned for 23rd - 24th February 2016 at Karlsruhe. It will comprise lectures, practical radiochemical training and a visit to a radioactive waste treatment facility. The course aims to provide an understanding of different $^{14}$C-containing waste stream, origins and hazards and their waste management.

Some aspects of WP7 are lagging behind the original schedule and it will be necessary to amend the schedule to reflect this as follows:

| Deliverable | Title | Current delivery month | Revised delivery month |
|---|---|---|---|
| D7.6 | Progress overview for Workshop1 (submission of scientific paper) | 20 | 28 |
| D7.7. | Overview of achievements on technical results for regulators for | 20 | 28 |

| | | | |
|---|---|---|---|
| | Workshop 1 (draft report) | | |
| D7.8 | Workshop 1 (logistics, announcements, documentation, brochures etc) | 22 | 27 |
| D7.10 | Workshop1 | 28 | 31 |
| D7.11 | Workshop 1 proceedings | 28 | 31 |
| D7.12 | Newsletter 3 | 28 | 31 |

# 8 Update on Work Package 1 (Coordination)

Twenty three of CAST’s deliverables had been completed and all the first year milestones had been achieved. An overview of the CAST project had been presented by the coordinator at the Nuclear 2015 conference held at Mioveni on 27th - 29th May 2015 and a paper based on the presentation has been submitted to the Journal of Nuclear Research and Development.

The CAST templates would be updated shortly to remove the FP7 logo and reword the acknowledgement to:

“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.”

Nagra had kindly offered to make arrangements for the next General Assembly Meeting, which will be held in Switzerland in October 2016.

# 9 CAST Beneficiaries Session

Steve Williams noted that he would be retiring at the end of 2016.

The following decisions were then agreed by majority votes of the CAST beneficiaries:

1. The re-scheduling of WP7 deliverables as described above in Section 7 – 21 votes in favour, no votes against.
2. The replacement of Steve Williams by Simon Norris as coordinator – 25 votes in favour, no votes against.
3. The possible addition of KORAD as a CAST beneficiary – 17 votes in favour, no votes against.

Steve Williams closed the meeting by thanking Daniela and Viorel for all their work in organising the meeting and all the participants for their contributions.

**Figure 1: Members of the CAST consortium at the General Assembly Meeting, Bucharest, October 2015.**