CArbon-14 Source Term

CAST

General Assembly Meeting 4 Minutes (D1.8)

26 – 27th October 2016

Luzern, Switzerland

Author(s):

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 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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General Assembly Meeting 4 Minutes (D1.8)

Executive Summary

The fourth General Assembly Meeting for the CAST Project was held on 26th – 27th October 2016 in Luzern, Switzerland. These minutes record the main points discussed at the meeting and serve to meet the objective of Deliverable D1.8 for the CAST Project.

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1 Introduction

1.1 *Welcome*

The fourth CAST General Assembly Meeting was opened by Steve Williams from RWM Ltd, UK. He welcomed the participants to Luzern, thanked Nagra for organising the meeting venue, and thanked the participants for the productive Work Package meetings the day before. Participants of the meeting gave a short introduction to themselves and their organisation's involvement in CAST.

1.2 *Attendees*

The attendees for the fourth CAST General Assembly Meeting were:

Table 1: Participants at the 4th CAST General Assembly Meeting

Name	Organisation
Tudose Aurelia	RATEN ICN
David Bottomley	JC Karlsruhe
Rachid Bouakkaz	Subatech/Armines
Guido Bracke	GRS
Sebastien Caes	SCK.CEN
Manuel Capouet	Ondraf/Niras
Benjamin Cvetkovic	PSI
Daniela Diaconu	RATEN ICN
Frank Druyts	SCK.CEN
Manuela Fulger	RATEN ICN
Vita Di Giandomenico	EdF
Irka Hajdas	Independent Expert
Jaap Hart	NRG
Tiina Heikola	VTT
Michel Herm	KIT
Camelia Ichim	RATEN ICN
Klas Kallstrom	SKB
Laetitia Kasprzak	CEA
Fraser King	Independent Expert
Solene Legand	CEA
Jose L Leganés	Enresa
Enrique Magro Lozano	Ciemat

Jens Mibus	Nagra
Ernestas Narkunas	LEI
Sophia Necib	Andra
Erika Neeft	Covra
Simon Norris	RWM
Olli Nummi	Fortum
Laurent Petit	EdF
Pascal Reiller	CEA
Corrado Rizzato	FZJ
Marina Rodriguez	Ciemat
André Rübel	GRS
Tomofumi Sakuragi	RWMC
Stéphan Schumacher	Andra
Ellie Scourse	MCM UK
Kastriot Spahiu	SKB
Tomo Suzuki	Subatech/Armines
Steve Swanton	Amec Foster Wheeler
Petr Vecèrnik	UJV Rez
Antonin Vokal	Surao
Erich Wieland	PSI
Steve Williams	RWM

2 Update on Work Package 2 (Steels)

Jens Mibus from Nagra gave an update on the work being undertaken in Work Package 2 on steels, including:

- An overview of the objectives and tasks for Work Package 2: Task 1 – the Literature Survey, has been completed; Task 2 – the analytical development, has also been completed; Task 3 – the corrosion experiments and measurements, is ongoing. Task 4 – the synthesis of results is currently being planned and will be completed towards the end of CAST.
- An overview of the progress made during the last year of CAST: a productive joint meeting with WP3 was held in June 2016 in Madrid. At this meeting discussions were focussed on the scientific and technical work, including analytical development, 14C modelling, finalisation of technical preparations and licensing, and the initiation of corrosion/leaching experiments.
- An overview of deliverables for WP2, including D2.6 Annual Progress Report for Year 3, which is being produced by Nagra, and should be finalised by the end of 2016.
- A brief update was given for work being undertaken in WP2, including:
    - Additional information from the State of the art report for WP2, including that the chemical form and microscopic distribution of Carbon and Nitrogen in steels will depend on the composition of the steel. Carbon and Nitrogen are predominantly distributed uniformly in solid solution in stainless steels and low carbon steels. In solid solution, chromium carbide formation may occur at grain boundaries. Carbon may form Fe3C phase or discrete phases of pearlite in carbon steel. The chemical form of C-14 in irradiated steels may be different from the bulk forms.
    - A brief overview of the analytical techniques developed by PSI were given, including the corrosion of iron in Ca(OH)2 versus NaOH solutions. The carboxylic acids show similar concentrations, whilst the hydrocarbons show a higher concentration in NaOH, which could influence the corrosion rate.

    - A brief overview of the decontamination and speciation analytical set-up developed by Subatech, to investigate solutions and resin treatments for decontamination.
- Corrosion experiments started in 2016 and an overview of results so far was given:
    - Amec FW/NRG – using 316L(N) austenitic stainless steel samples - 1 unirradiated, 2 irradiated. The samples were leached in 600 ml 0.1M NaOH (pH 13) under N2. A hot cell was used due to a high dose rate. Initial results show that 14C release in solution phase has fast initial release, then rate decreases. Speciation is not clear. Initial results show that 14C release in gas phase has fraction of release - 1 to 10% of the released 14C and is predominantly hydrocarbons (CH4).
    - PSI – inactive test – two types of experiments – solution exchange and iron exchange. Also corrosion experiment with activated steel – 'hot' experiment with two activated steel nut segments. Initial results show that the total dissolved 14C is detectable and that a linear increase is observed (total dissolved = organic fraction). Single 14C-fractions have not been detectable so far (dilution due to separation).
    - KIT – dissolution experiments – dissolution of stainless steel subsamples in a shielded box using an autoclave. Preliminary results show that ~99% of 14C as gaseous/dissolved hydrocarbon or carbon monoxide.
    - RWMC – corrosion rate of non-activated stainless steel – corrosion tests of stainless steel by H2 measurements investigating the effects of temperature and solution (pH). Initial tests undertaken using pH12.5 >/~ deionised water.
    - SCK.CEN – corrosion of mild steel – static test with activated C-steel started on 7th July 2016 and expected to last 6 months, with no interim sampling. Accelerated tests are still in preparation.
    - VTT – active experiments using surveillance capsule material from the Loviisa reactor (radiation exposure from 2011 – 2015). Two leaching experiments undertaken at pH 8.5 and 12. Experiments started in June 2016 and will last 3 -6 months. Analysis from liquid phases still in progress.

    - Ciemat/Enresa – leaching under aerobic conditions. After a blank test, the leaching process started in June 2016 with two samples under aerobic conditions. Renewal of both gas and leachate after 14, 28, 56, 90, 180 and 360 days (up to 90 days completed). Gas samples analysed directly, leachant stored for later analyses. The data is currently being processed.
    - JRC – preparation of samples still underway, re-testing of stainless steel cladding samples (NIMPHE fuel). Preparation of stainless steel ring samples for testing – experiments due to start in December 2016 and take 3 months to carry out.
- An overview of the activation calculations was given, including:
    - Nagra, KIT, SCK.CEN (and LEI) will be modelling samples and will then compare them, with support from the experimental groups. The estimation of uncertainties in the inventory will be made. Currently have fewer samples than expected, and not as much progress has been made as planned. However, some calculations have been undertaken with input (irradiation data) from Enresa/Ciemat, ITU, KIT and VTT. Nagra is doing a consistency check. An example was given from the KIT KKG fuel activation calculations for stainless steel and zirocaloy. The results are quite promising and the experimental and calculated results agree within 50%. The uncertainties are quite large – especially for nitrogen content in stainless steel. New calculations are likely using SCALE 6.2 and also the implementation of 3D models.
- An overview of the present understanding as a ‘working hypothesis’ was given:
    - Activation of stainless steel samples from reactor internals occurs in the bulk metal and the oxidation layer (the thickness of which increases quickly);
    - Activation of N14 and a smaller but significant contribution from O17 are assumed;
    - The 14C speciation is dominated by carboxylic acid (formate, acetate) and smaller amounts of hydrocarbons (methane);
    - The entrapment mechanism is not clear;

  - After immersion in the leachant, the readily available fraction of 14C is released instantaneously (approximately one week into the experiments), and is dominated by carboxylic acid;
  - Later the release rate is reduced – we presume that the speciation may change to hydrocarbons, however the availability of oxygen due to radiolysis is not clear;
  - In the long-term, 14C is slowly released from the bulk, the rate of which can hardly be determined within the CAST project.
- Preliminary conclusions were discussed:
  - Corrosion/leaching experiments have been started in nearly all labs.
  - First results indicate a fast instant release of 14C, mainly carboxylic acids to the aqueous phase, which can be interpreted as a small IRF (less than 1%).
  - The long-term rate is much lower but difficult to measure in CAST lab experiments. The speciation is not yet clear.
- The outlook for WP2 includes the continuation of corrosion/leaching experiments until Spring 2017. A joint WP2 and WP3 meeting will be held in March 2017 in France. There will be a WP2 data freeze for the submission data to WP6. Draft reports on experimental data expected by the middle of 2017.

Jens closed the WP2 session by inviting participants of CAST to the Clay Conference 2017 meeting in September 2017 in Davos, Switzerland.

Some of the main discussion points for WP2 are captured below:

- Some of the experiments in WP2 are single samples, so that any results that you see for instant release fractions is a ‘snap-shot’ in time. Often the fast initial release happens over the first few weeks, so long-term rates are hard to measure. For such quick instant release, then this becomes a waste packaging/operational issue, and may not impact on post-closure.
- For the one point experiments it is difficult to measure that the 14C release is concurrent with corrosion. It takes a long time for it to settle into the long-term rates after the quick initial release. Cobalt could possibly be used to help this, but it may also be affected by other mechanisms (sorption etc.).

- Detailed understanding of experiments is required – how does nitrogen dissolve in steels? Is it homogeneous? Is it crystallised or single atoms when it is converted to carbon? However, it was noted that in CAST we are focussing on experimental development, and need to focus on overall experimental uncertainties and the inputs of these into WP6.
- For WP6, two different assumptions may be useful – one for the expected behaviour supported by expert judgements, and another as a pessimistic estimation based on uncertainties.

3 Update on Work Package 3 (Zircaloys)

Sophia Necib from Andra gave an overview of the status of WP3 Zircaloys. The objectives for WP3 were presented, along with an overview of the Tasks, contributions from WP3 partners, the WP3 programme, and WP3 deliverables for Year 3 of the project.

A brief overview of the results from Task 3.1 were given, including from D3.1 'State of the art of 14C in Zircaloy and Zr alloys – 14C release from Zr alloy hulls'. This deliverable gave a history of Zr alloy claddings, the environment assisted release of 14C, the inventory of 14C and the speciation of released 14C. A brief overview of the literature review was also given, including some of the key results for 14C release in aqueous solutions. A significant part of the 14C activity has been identified as being in the external layer of the cladding. The outstanding issues outlined include:

- Inventory of 14C – comparison between modelling and measurements, and 14C speciation into the metal and into oxide layers.
- Corrosion of Zircaloy at low temperatures
- Dissolution rate of ZrO_2
- Leaching – in particular the role of thermal diffusion of 14C in the ZrO_2 layers and other possible mechanisms of migration; and chemical forms of 14C released.

An overview of the materials being considered in WP3 was given, including non-irradiated Zr, irradiated Zr and their microstructures. Their properties were compared: for non-irradiated samples this included the Zr alloy type, chemical composition, metallography, pre-treatment of surface specimen, oxide thickness. For irradiated samples this included the Zr alloy type, chemical composition, microstructure, activation history, 14C inventory, and pre-treatment of the specimen.

An overview of Task 3.2 was given outlining the analytical strategy for each of the experiments by participants in WP3. The set-up for the leaching and corrosion rate experiments were given, including a comparison between the experimental set-up by each participant, outlining the sampling (gas/liquid), techniques used and aims of the techniques.

For the leaching experiments/corrosion rate measurements the experiments by CEA, KIT, JRC/ITU, RATEN.ICN, RWMC and SCK.CEN were overviewed including details on the pH, temperature, porewater, O2 measured and duration of the experiment for leaching solutions of unirradiated and irradiated materials. An overview of the current results was given for each of experiments.

Corrosion rate measurements of unirradiated materials has only been developed by a few participants – SCK.CEN, ITU/JRC,RWMC and RATEN ICN. This is a very difficult process to measure due to such low rates. Some of the current results were presented.

A detailed presentation by Solene Legand (CEA) was given on the details and results of the leaching experiment and 14C analysis in liquids:

- Leaching experiment performed at CEA, with the aim of undertaking leaching tests under de-aerated alkaline conditions on selected Zr-alloys. These tests were carried out in the hot cells of the ATALANTE facility (CEA Marcoule).
- Materials – hull coming from La Hague reprocessing facility (Areva) – an overview of material characteristics was given. Materials characterised by Raman spectroscopy.
- Leaching experimental conditions presented – 2 samples taken at 14 days and 6 months. Preliminary results have been previously presented for the samples removed after 14 days. The results for the samples removed after 6 month are new.
- An overview of the CEA analytical strategy was given, including techniques developed for analysing carbon mass balance and organic speciation.

- For total 14C and partition - the results indicate that there is no evolution of 14C released in leachate between 14 days and 6 months. AMS – quantification of total 14C at low level to compare and validate with LSC, additional results will be obtained in November.
- For total carbon the ‘inorganic’ conclusions are that all peaks called ‘artefacts’ in previous presentations have now been identified as inorganic compounds, including carbonate. There is an increased total inorganic carbon content but the carbonate concentration is approximately the same between 14 days and 6 months – perhaps indicating a carbon source in solution? For total carbon the ‘organic’ conclusions are that the contamination from formiate ions – higher concentration in the NaOH than in leachates. Increase in 3 organic compound concentrations between 14 days and 6 months.
- For carbon mass balance the broad conclusions at this stage are that there is no evolution between 14 days and 6 months, and that the overall 14C concentration is very low.
- Going forward CEA will focus on:
  - AMS validation to compare with results in LSC;
  - Organic compound speciation by GC-MS – tests in progress, but depends on sample preparation for highly concentrated alkaline solutions;
  - Leaching experiments – last leachate sample analysis – these should be finished by March 2017.

A detailed presentation on leaching experiments, 14C analysis and CR measurements at RWMC was given by Tomo Sakuragi (RWMC). An overview of Task 3.3 was given, including source term issues in the safety case, 14C specific activity measurement for irradiated cladding, leaching tests using irradiated cladding, and conclusions from the RWMC studies.

- Source term issues for spent cladding (hull), including an overview of 14C release source after disposal, and that the oxide layer has been regarded as a source of the instant release fraction.

- An overview of the 14C specific activity, and measurement for irradiated fuel cladding was given, including the sample overview and a description of the recovery of hull oxide
- An overview of 14C measurement system was given, outlined the wet oxidation analysis for 14C including an overview of the procedure. Results were presented of 14C in the oxide layer. The results roughly agree with the previous Japanese calculations from ORIGEN, that suggest that 14C in oxide is ~3.5%, therefore the current assumption in the Japanese safety case of 20% IRF is somewhat conservative.
- An overview of the static leaching test with NaOH solution and Ph 12.5 was given and results presented after leaching 14C for 6.5 years. The total leached 14C is 0.0038% which is comparable to the previous short term test that also showed less than 0.01%.
- The estimation of 14C release from oxide was presented by a conceptual representation to try and determine where the 14C comes from within the oxide. Zircaloy matrix corrosion related to congruent release. The oxide layer is dominant in the 14C release from irradiated cladding.
- Conclusion from the RWMC study show that:
    - The 14C specific activity in the external oxide is 2.8 times that in base Zircaloy, however the 14C distribution in the oxide layer is only ~7.5%
    - Oxide layer is dominant in the 14C release, nevertheless the total 14C over 6.5 years was less than 0.01%.

Sophia highlighted that the outstanding uncertainties that will be considered in WP3 are:

- Impacts of hydrides on CR
- Inorganic/Organic partition – pH influence
- Dissolution of ZrO2
- Stability of compounds
- Instant Release Fractions.

Sophia outlined that 2017 will be devoted to finishing the experimental and modelling work for Task 3.3 and Task 3.4. Seven deliverables will be slightly postponed. A progress meeting will be held in conjunction with WP2 in France in Spring 2016 to finalise and synthesise the experimental work.

Some of the main discussion points for WP3 are captured below:

- There are a lot of uncertainties surrounding the Instant Release Fraction, normally this is assumed to be approx. 20%, but this is based on conservative assumptions and needs to be clarified. It was outlined that it is not the objective of the experimental tasks to define this value. The experiments can provide data, but the development and interpretation of the Instant Release Fraction included in the safety case should be part of WP6.
- There are also a lot of uncertainties about the rate of congruent release. This appears to be congruent with the corrosion rate, but this should be confirmed with the leaching experiments. Potentially the experiments are too short to demonstrate this, accelerated experiments would be the only way to demonstrate this. For WP3 it should be possible to make estimates, but this would remain an uncertainty.

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

Pascal Reiller from CEA gave an overview of the status of WP4. The objectives for WP4 were presented, along with an overview of the contributions from WP4 partners, the WP4 Tasks.

There are two delays, one due to FZJ experiencing experimental issues, and another due to a delay in the transfer for an EdF sample from Cadarache to Saclay.

There was a WP4 interim technical meeting in Bucharest on 13th – 14th June 2016. A selection on interim results were presented by WP4 participants from CEA-EdF, UJV and FZJ.

CEA-EdF Carbon-14 Source Term CAST by Laurent Petit:

- Laurent gave an outline of the samples and methodology adopted by CE-EdF, including an outline of the 14C inventory and 14C speciation.
- The origin of spent ion-exchange resins was discussed, including that EdF operates 58 PWRs in France, and that IERs are used for purification of various circuits, and that there are a combination of cationic, anionic and/or mixed bed resins depending on the function of the IER.
- The operating histories of the SIERs from France were discussed, including the discharge conditions, and sampling overview. Laurent reminded that the samples are representatives of the waste before conditioning (not of packaged waste). An overview of the SIERs delivered to CEA was given, and it was highlighted that there was a visual difference between the SIERs, and that the dose rates varied hugely between the samples (due to different origins and storage delays).
- The analytical method developments were described in detail, including the total 14C by combustion with O2, and the speciation of 14C by acidic mineralization. The two analytical methods were then compared, concluding that the combustion method lead to consisted results and high carbon rate recovery (>95%). An important loss of 14C is shown using the acidic dissolution method – the method is not adapted for dried samples.
- A synthesis of the 14C measurements was given, including outlining that the aim of the project has been achieved (total 14C measurement in SIERs), but it is difficult to compare wet SIERs.
- 14C speciation was discussed – up to now only one result is showing 75% of mineral carbon-14 (another experiment is in progress). A question remains about the representativeness of the results – more samples need to be analysed and a statistical analysis needs to be undertaken.
- Carbon-14 desorption experiments were performed to produce a liquid phase with the radiocarbon coming from the SIERs with the aim of identifying the carbon-14 bearing organic molecules. The results from this experiment were presented and some questions are outstanding – the incomplete carbon-14 balance (carbon-14 loss in the gas phase?) and the stability of organic molecules at pH 14 (mineralization process?).

- The identification of carbon-14 bearing organic molecules is currently being worked on, using three analytical techniques: total carbon analyser (quantification of total inorganic and organic carbon), ion chromatography (quantification of small carboxylic acids) and gas chromatography – mass spectrometry (identification of low volatile molecules).
- To conclude, more studies are need on the analytical method development (for acidic dissolution methods on dried SIERs), on statistical approaches to investigate the representativeness of the samples, and on the choice of the desorbing conditions for carbon14 bearing organic molecules.

UJV Rez gave a presentation on their work in the CAST Project, including:

- An outline of UJV Rez and the nuclear facilities in the Czech Republic.
- An overview of the objectives for UJV Rez in the CAST project – to measure the amount of carbon-14 released from ion exchange resins and their solidified forms to water during leaching tests. After the development of required equipment and verification of methodologies, experiments were conducted to find the maximum rate of carbon released.
- Tests were focussed on carbon release from simulated ion exchangers, with organic (simple organic acid) and inorganic (carbonates) forms of 14C, followed by tests using real samples from nuclear reactor operations. Following this, the release of carbon14 after the fixation of ion exchange resins into the solid matrix was studies. In this step, simulated and real samples will be tested.
- An overview was given of the:
  - materials, including the 14C solutions and the ion exchange resins,
  - non-active tests
  - equipment used for 14C activity measurements
  - 14C experiment details
  - Cement matrix preparation and testing
  - 14C desorption experiments
- A summary of the results to date were given, including those from the leaching of fixed resins (cement matrix) and it was concluded that there is no measurable release

of 14C observed during the leaching tests of fixed resin into the cement matrix. Due to this is was not possible to evaluate the leachability or diffusivity of fixed 14C.

- The work left to do for UJV include continuing with long-term tests, undertaking experiments with organic 14C tracers, investigating the fixation of real SIERs to the cement matrix, and leaching experiments.

FZJ gave an overview of the Radiocarbon on SIERs arising from BWRs, by Corrado Rizzato:

- The presentation gave an overview of the sample selection used by FZJ.
- The 14C inventory and speciation in SIERs analytical approach was summarised, including the method for total 14C (combustion with chemical oxidation of released species), and the method for inorganic/organic 14C (acid regeneration and wet oxidation). Results show that the numbers do correlate roughly between the methods and that the differences could be statistical, or due to particulate matter.
- Morphological studies were discussed, where some agglomerates containing iron and cobolt were presented, the agglomerates could retain 14C?
- 14C release from SIERs and its speciation in aqueous and gas phases were presented – including the influencing factors.
- Results from storage experiments were shown, the release of 14C could be influenced by equilibrium with water/atmosphere or by temperature. There was a strong release of inorganic 14C depending on the samples age – radiolytic effects did not seem to be significant for these samples.
- Results from leaching experiments were shown, with deionised water did not see any release, but with cement pore water (high Ph) did get strong release of gas, however these results have not yet been verified.
- The simulation of radiolytical effects in SIERs including the degradation mechanisms of fresh and loaded IERs was presented, and showed a good agreement with the literature for fresh resins. For loaded resins, the mechanism seems more complex.
- The correlation between the experimental and theoretical data was discussed and it was concluded that the missing link is the validation of SIERs.

- To conclude:
  - Total, organic and inorganic 14C evaluation – organic fraction 0.3 – 0.4%;
  - Formic acid in small amounts, perhaps arising from the coolant from the degradation process?;
  - Organic 14C is probably in exchangeable form;
  - Storage experiments showed an 'ageing effect' and temperature effect on the release of 14C and the 14C release seems to correlate to residual exchange groups (work still ongoing);
  - The 'ageing effect' seems to be predominant over the radiolytic effect, at least for the measured samples;
  - The leaching tests showed that with deionised water there were no detectable releases, on-line tests in an open system revealed significant releases in a short time. With high pH there seemed to be fast 14C release in the gas phase, but verification of these results is required.
  - The study of radiolytical effects on model materials showed enhance release and new species with loaded resins, and that formic acid in solution may be linked to SIERs. The mechanisms for radiolytical degradation seem complex.
  - The Molecular Dynamic simulation explain some of the primary degradation mechanisms of IERs.
  - Validation of real waste ion exchange capacity as an indicator of the absorbed dose/degradation of the resins – predication of waste behaviour.

To conclude for WP4, Task 4.4 was summarised, which includes the synthesis of experimental data and interpretation; the development of interpretation of 14C behaviour from SIERs; summarizing and synthesising the experiment studies into the final interim report, and the final WP4 meeting.

5 Update on Work Package 5 (Graphite)

Simon Norris from RWM, gave an overview of WP5 including an introduction to the WP5 participants, the WP5 objectives, tasks, and key deliverables – both those delivered and those still to come. A selection of WP5 presentations were then given by various participants.

RATEN ICN work progress on TRIGA i-graphite by Camilia Ichim:

- Overview of proposed activities for ICN in WP5 – 14C inventory in TRIGA i-graphite, and leaching tests of TRIGA i-graphite (geological disposal conditions and 14C released in liquid phase and its partitioning between inorganic and organic fractions)
- Overview of TRIGA research reactor, including the thermal column design, and samples of i-graphite from reactor taken from cylindrical bars. First leaching tests on TRIGA i-graphite.
- Overview of methodology for total 14C measurements – non-catalytic combustion by flame oxidation method using LSC.
- Tests of labelled graphite – virgin graphite labelled with 14C with the objective to optimize the total mineralization process with total recovery of 14C. The details of the experiment were given and 97% 14C was recovered. Initial results for total 14C measurements show good reproducibility.
- Leaching experiments – two performed under aerobic conditions, solution samples analysed using LSC for 14C activity measurements. Experimental conditions for leaching tests were outlined.
- Preliminary results were outlined.
    - **Inorganic and organic 14C measurements** – a little late due to delay in getting equipment, but is being set up now. Uses acid stripping and wet oxidation.
    - **14C recovery** – shows that some tests seem to transform part of the organic 14C.
- The work that still has to be undertaken was shown including: tests to optimise the acid stripping process, test on solutions sampled from the leaching test to determine total 14C and inorganic/organic carbon, and to continue the anaerobic condition leaching tests.

WP5 Annual Progress by Andra and EdF by Laurent Petit:

- Overview of the French context for graphite and the contributions for EdF and Andra to WP5, including their deliverables D5.1 and D5.8. This is an overview of D5.8 – 14C leaching: speciation in the leaching liquid and in the gas phase.
- An overview of the D5.1 conclusions were given, specifically that more experiments are needed, and that the results obtained on French i-graphite cannot be directly compared to other nuclear i-graphite. 14C behaviour is dependent on operational history and background of each sample.
- A summary of D5.8 was given, including:
    - An overview of material description and sample history and characterisatics.
    - An overview of leaching test parameters and apparatus used in experiments.
- The main results from D5.8 show that:
    - Very low 14C release in the gas phase depending on the graphite sample – less that 0.1 – 0.01% of 14C total inventory released to gas phase after 1.5 years. Representative of crushed samples? 14C lost during crushing?
    - In the liquid phase around 30 – 35% of the 14C is released as organic compounds for all the samples tested. Nature and origin of organics is undetermined – effects of pH?
    - Influence of pH – not possible to conclude at this stage (because a change of graphite particle size distribution was observed at pH13 – agitation effect or pH effect?) - further tests are required to complete the analysis.
    - Influence of particle size – changes in particle size distribution for the experiment carried out at pH 13 with continuous agitation – increase of 14C due to size differences, pH or continuous agitation?
- Conclusions
    - 14C release rate very low - need to adapt the leaching experimental parameters in order to increase carbon-14 concentration in the leachate and gas phase;

- In high pH conditions organic 14C release is observed in gas phase – around 30-35% in liquid phase is organic – this is consistent with previous results from UK i-graphite?
- The influence of experimental parameters need to be clarified.
- 14C release rate values cannot be used for disposal conditions, (i-graphite will not be powdered for disposal, continuous agitation etc.). More studies needed to collect data suitable for release rate model in disposal conditions.

There was discussion about the results from this presentation, these are summarised below:

- What would the experiments look like to make it applicable to disposal conditions? Chunks of graphite? If use this then the levels of 14C would be so small that you would not be able to measure them. Have to change the experimental conditions in order to accelerate the process to be able to measure 14C.
- There was in depth discussion around nitrogen and 14C generation.

Simon Norris outlined that not all participants in WP5 are investigating leaching, for example ENEA are considering exfoliation. Simon also noted that the Ukrainian contribution to the project needs to be considered further.

6 Update on Work Package 6 (Safety Assessment)

Manuel Capouet from Ondraf/Niras gave an overview of WP6, including the WP6 technical meeting in March 2016 in the Nagra offices in Switzerland. At this meeting, the WP2 – WP6 presented their immediate and expected results and experimental conditions, and how the laboratory results may be applied to disposal conditions. There was also a selection of topical presentations. Manuel continued by giving a detailed overview of the status of WP6 deliverables, including that D6.2 is under review and should be finalised shortly. The delivaeble on the ‘Impact of Microorganisms on 14C speciation and migration’ is in draft form and ready for review. D6.3, the Interim progress report, requires national programme contributions on the integration of CAST results in the safety case. D6.4 is the final deliverable for WP6, and Manuel gave an overview of the planned structure of the report.

Sensitivity/uncertainty analysis was discussed to anticipate the impact of the CAST experimental outcomes. Some of the key factors that could be analysed are: 14C activities in waste types, corrosion rates, instant release fraction vs. congruent release, etc.

Manuel concluded by giving an outlook on the WP6 work, including an abstraction session at the WP2/3 technical meeting in April 2017, where by the data from these WPs will be 'frozen' to allow for WP6 analysis. The next WP6 technical meeting will be help in May 2017, and will aim to continue the abstraction of data to geological concepts.

As part of the WP6 session, Andra, Fortum and NRG all gave detailed overviews of how 14C is currently managed in their safety cases.

7 Update on Work Package 7 (Dissemination)

Erika Neeft from Covra gave an update on WP7, including:

- That there were 37,000 hits to the website in 2016, including 8882 unique visitors. This means the website is being well used and found by people other than those in the project.
- There was discussion on dissemination, specifically group specific dissemination, explaining that the newsletters are aimed at the layperson (general public), the training courses (entry level, early career) and finally workshops (detailed).
- There were 5 newsletters planned on 5 topics based on scheduled publications in WP2 – 6. The 1st has been published and the 2nd and 3rd are in progress.
- Training courses, aimed at early-career researchers, the first was held in 2016 and organised by KIT, but there were problems with getting attendees of the required level – most of 8 attendees were quite well developed in their careers – not early career/students. The second training course will be organised by Covra and should be held in December 2017.
- Workshops are aimed at experienced researchers with a responsibility for the implementation of radioactive waste management/disposal. At each workshop there should be a waste generator, waste organisation and a regulator for each European country. This equates to 16 countries with NPP in Europe, and Poland, Switzerland,

Japan and Ukraine were also invited. The first workshop was well attended by WMOs - 75% of EC states. Fewer regulators and only 2 waste generators attended.

- At the first workshop, WMOs presented inventory data for 14C – amount of wastes (steels, zircaloy, SIERs) and what the designated end-point of the waste.
- If there is a second workshop then it will be organised by LEI and Covra. Invitations will be sent out in January 2017, with the aim of getting 9 EU countries, with a mix of WMO, regulator and waste generator attendance.

The main discussion point related to whether the second workshop could be held in conjunction with the final CAST symposium in January 2018?

8 Update on Work Package 1 (Coordination)

Steve Williams from RWM led discussion for WP1, including an overview of:

- CAST objectives, including a reminder that the project should focus on improving understanding of 14C generation from particular waste materials and disseminating this knowledge.
- CAST Deliverables and Milestones for Year 1 (11 deliverables and 6 milestone achieved), Year 2 (12 deliverables, no milestones due, 6 deliverables outstanding) and Year 3 (lots of deliverables due, and a lot due to be delivered soon). An outstanding milestone for Year 3 is the submission of scientific paper at international conference. A suggestion was a submission to the Clay conference in 2017? In Year 4 a significant number of deliverables are due, including bringing the technical details to completion and the synthesis of technical work.
- Some more detailed points discussed for WP1 included:
    - Reporting for the 2nd EC Reporting Period now underway – all Form C's submitted by 15th November 2016.
    - Some experiments have been delayed, which may impact on final deliverable dates, but should not impact on the overall completion of CAST.

- The Coordinator of CAST will change from 2017 onwards, as Steve Williams retired. Simon Norris will take over as Coordinator (subject to approval from the EC).
- There is a suggestion that we change the final General Assembly Meeting for CAST into a symposium/conference, to allow wider dissemination of the results to colleagues outside of the project (subject to approval from the EC).