EUROPEAN COMMISSION

European Research Area

# CArbon-14 Source Term

# CAST

## Workshop 2 Proceedings (D7.21)

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|---|---|---|
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| **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 as dissolved and gaseous species from irradiated metals (steels, Zircaloys), irradiated graphite and from ion-exchange materials as dissolved and gaseous species.

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

The objectives of the CAST project are to gain new scientific understanding of the rate of release of carbon-14 from the corrosion of irradiated steels and Zircaloys and from the leaching of ion-exchange resins and irradiated graphite 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: 7 | CAST Document no. : | Document type: R |
| Task: 7.4 | CAST-2018-D7.21 | R = report, O = other |
| Issued by: JRC | | Document status: |
| Internal no. : | | Draft/Review/Final |

| Document title |
|---|
| Workshop 2 Proceedings |

## Executive Summary

The report summarized the outcome of the second workshop of the CAST project. The two-fold aim of this workshop was to present the results obtained and to discuss the outcomes with regulators, waste management organisations and waste generators. The results obtained have been presented at the CAST Final Symposium and therefore the second workshop was organised in conjunction with this symposium.

For these stakeholders with a responsibility in the management of radioactive waste, contributions have been requested for the workshops. The regulators were asked to prepare themselves by reading a report "Overview of achievements for regulators workshop", issued about a month ahead of the workshop. A time slot was reserved for the waste management organisations at the end of the CAST Final symposium to express their point of view of the implications of CAST Project outcomes on safety assessments. The contributions by the waste generators were intended to increase the reliability on characterisation of carbon-14 containing waste but since their contribution in the first workshop was limited, the waste management organisations were asked to provide these details for the types of waste investigated in CAST. The workshop focussed on assessing the above-mentioned report, presented and discussed information provided by participating Member States on the origin, quantities, release mechanisms under repository conditions, and the resulting $^{14}C$ dose source term. Finally, three questions concerning the nature of the project outcome and the way ahead were discussed:

1) Does the R&D status show divergence or convergence of knowledge?

2) Is the R&D outcome providing comfort to already existing solutions or improvements to concepts?

3) How to move ahead?

The present status is that the key mechanisms are understood, or that the key questions are identified i.e. there is not the expectation that new knowledge will open up new uncertainties. There is potential left of turning the R&D outcome into achieving practical improvements but that will require time but also of improved involvement of exchange with waste generators. Waste characterisation is the key for a future solution and joint solutions offer a possibility for small inventories to be managed adequately up and until the management end-point.

# List of Contents

# 1 Introduction

Two workshops have been held within the CAST project. The workshops were envisaged to implement the new understanding of the potential release of carbon-14 from radioactive materials under conditions relevant for waste packaging and disposal to underground geological disposal facilities since the scientific progress is already evaluated by the Advisory Group and results obtained in CAST have been and will be presented in scientific fora. For this implementation, stakeholders with a responsibility in radioactive waste management were envisaged. The first workshop had a threefold aim: to disseminate the initial findings, let these stakeholders become acquainted with the proposed research and to allow sufficient opportunity for questions. This workshop has taken place on 5 and 6 October 2016. The second workshop had a two-fold aim: to present the results obtained and to discuss the outcomes with the regulators, waste management organisations and waste generators. The second workshop has therefore been organised in conjunction with the Final CAST symposium and held 18 January 2018 in Lyon since the obtained results were presented there.

The workshop had four topics:

1. Evaluation of regulators second overview technical achievements
2. Contributions of participating countries
3. Understanding potential $^{14}C$ release mechanisms, and
4. Wrap-up with discussion of a series of questions

The different topics are briefly discussed below.

# 2 Evaluation of regulators second overview technical achievements

For the second workshop, the documentation for regulators is published as CAST D7.16. The rationale behind involvement of the waste management organizations, waste generators and regulators is essential in order to, amongst others to:

- Obtain information from those who generate the waste in order to understand the underlying processes, and direct research in the right direction in view of identifying possibilities for:

- lowering the conservatism through improved essential data used for dose estimations/calculations,
- reducing the $^{14}C$ waste generation, including the $^{14}C$ inventory in the waste,
- treating the waste in order to reduce the quantities of $^{14}C$ containing waste material,

- Exchange with regulators on how to promote such developments.
- Exchange between those who generate the waste for identifying and implementing improvements.

The discussion revealed that the “Overview of achievements for regulators for workshop 2” (D7.16) provided a comprehensive overview of the processes leading to generation of $^{14}C$ waste, including formation processes and presence of $^{14}C$ in the four important source materials, namely steel, zircaloy, ion-exchange resins and graphite, together with the $^{14}C$ release mechanisms, speciation and disposal source term. The report was found very important and comprehensive, with no specific recommendations on further actions.

# 3 Contributions of participating countries

For the contribution to CAST in the second workshop, each participating country presented information on potential $^{14}C$ waste sources. This included material with its origin in reactors, namely, steel, zircaloy and graphite. For these potential sources, the following questions were asked:

- What is the nitrogen content?
- How is the nitrogen content determined / specified?
- What is the neutron irradiation period and thermal flux?

$^{14}C$ waste is also generated from the purification of reactor coolant by ion exchange. For the resulting spent ion exchange resins having scavenged $^{14}C$ containing ions, the following questions are asked:

- Is there control of air ingress into the coolant?
- How is the pH of the coolant controlled?
- Is the $^{14}C$ activity concentration measured?

The presentations responding to these questions are provided in Annex I. This information is summarized in Table 2.1, including an overall indicative overview in the last row of the table. More detailed information can be found in the report CAST D7.16.

Table 2.1: Overview information for $^{14}C$ waste from countries participating in the survey. Details can be found at the CAST web page (https://www.projectcast.eu/training/workshops)

| Country / | Type of reactors | | Irradiated Steel | | | Irradiated Zircaloy | | Spent ion-exchange resins | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Information source | Power (thermal/ electric (GW)) | Neutron flux (thermal, $cm^{-2}s^{-1}$ ) | Neutron irradiation period | Origin | Nitrogen content | Origin and Nitrogen content | Neutron irradiation period | Coolant air ingress control? | Coolant pH controller | Waste treatment | C-14 content Measured? | C-14 specification measured? | I-Graphite |
| NL / COVRA & EPZ | 1.366 / 0.515 | : $8x10^{13}$ – (reactor core), $2x10^{12}$ (vessel wall) | 4, 21 and 31 years | Grid supports, ducts etc. | Assumed to be comparable with other Siemens reactors; not listed in vendor specification | Zircaloy M5 (PWR) claddings: Vendor (AREVA) does not specify | Not relevant, inventory after reprocessing is the same as disposed in | 1 ppb $O_2$ | Primary circuit: LiOH Secondary circuit: Hydrazine | Evaporator drying with sludge. | No | No | No graphite in EPZ NPP |
| BG, SERAW | VVER 440 / V-230, 0.44 GWe | : $7x10^{13}$ – (reactor core), | Based on fuel cycles | Cladding, grid support, shaft, basket, ducts, etc. | Reactor core: Not specified | Claddings: Not specified | Not relevant as claddings will remain in Russia after reprocessing | Controlled | KOH / $NH_4OH$ | Drying by bubbling, Conditioning not specified | LSC after oxygen combustion | No | No graphite |
| FI, Fortum | VVER 0.5 GWe | $10^{13}$ core average | 50 a (less if replaced) | Shield elements, reactor pressure vessel, grid support | 0.04 – 0.14 % (vendor specification) | Claddings: 10 – 30 ppm | 3 – 4 a | Likely yes | Boron / Ammonia | Fluid with resins cement solidification in concrete containers | Yes: Combustion and acidic dissolution | Yes | No graphite |
| HU, Paks NPP | 4 x VVER | $5\text{-}7\times10^{13}$ | | Cladding/ other (grid | 0.05 wt% | Claddings, | 4 × 15 months | Yes | Hydrazine | Drying (not specified) | Yes, | Yes | Not in the Paks NPP |

| Country / | Type of reactors | | Irradiated Steel | | | Irradiated Zircaloy | | Spent ion-exchange resins | | | | | I-Graphite |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Information source** | **Power (thermal/ electric (GW))** | **Neutron flux (thermal, $cm^{-2}s^{-1}$ )** | **Neutron irradiation period** | **Origin** | **Nitrogen content** | **Origin and Nitrogen content** | **Neutron irradiation period** | **Coolant air ingress control?** | **Coolant pH controller** | **Waste treatment** | **C-14 content Measured?** | **C-14 speciation measured?** | |
| | Each 0.5 GWe | | | support, ducts et cetera) | Vendor specifications or own measurements | Max. 0.06 wt% | | | | | Transport water is measured by chemical separation and LSC. | | |
| ES, ENRESA | PWR: 1 GWe<br>BWR: 0.16 GWe | $4x10^{13}$ (core) – $4.9 \times 10^{9}$ (vessel wall) | Vessel, internal components: 455 months<br>Fuel elements:<br>4 to 6 years | Of fuel elements:<br>PWR=><br>Top nozzle, plenum spring<br>BWR=><br>Top nozzle, plenum spring, expansion spring | SS-304: 1000 ppm<br>Carbon Steel: 84 ppm | Claddings & Fuel element components:<br>PWR:<br>Grids and guide tubes<br>BWR:<br>Grids and fuel channels<br>Nitrogen content:<br>Regulatory limits =><br>80 ppm | 4.5 – 6 years | No information | Probably LiOH for PWR | Fluid with resins bubbled and/or dried?<br>Decantation | Yes<br>Combustion with oxygen and liquid scintillation ($^{14}C$ and $^{3}H$) | No | Vandellós I: Graphite Gas Cooled Reactor<br>Expected neutron irradiation period for<br>Moderator: Power plant life 17 years<br>Sleeves: fuel life |
| SI: Nuklearna Elektrarna Krško | PWR<br>1.994 GWt<br>0.727 GWe | $3x10^{13}$ | Average 1100 days | Fuel assembly components | Max 0.1 wt% | Cladding Assumed < 40 ppm | Average 1100 days | Yes | LiOH | - | No | No | None |

| Country / | Type of reactors | | Irradiated Steel | | | Irradiated Zircaloy | | Spent ion-exchange resins | | | | | I-Graphite |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Information source | Power (thermal/ electric (GW)) | Neutron flux (thermal, $cm^{-2}s^{-1}$ ) | Neutron irradiation period | Origin | Nitrogen content | Origin and Nitrogen content | Neutron irradiation period | Coolant air ingress control? | Coolant pH controller | Waste treatment | C-14 content Measured? | C-14 specification measured? | |
| FR: ANDRA | | | | | | Claddings: Zircaloy 2 (BWR) (ppm): Specification: <80, Zircaloy 4 (PWR): Specification: <80 Analysis of castings or tubes: 27±4, and 34±10 | | | | | | | Bugey Reactor: Neutron moderator (10-24 a), Sleeves (5-10 a) biological shielding<br>Coolant Gas: $CO_2$ or air, ≈ 200 – 500 °C<br>Mainly activated $^{13}C$ (Nitrogen to a lesser degree)<br>Source of Nitrogen: Carbonated materials from manufacture, air in graphite pores, impurity in gas coolant & air inflow from maintenance |
| Indicative overview | <u>Neutron flux:</u><br><br><u>Core:</u><br>Thermal: 3 - $8x10^{13}$<br><br><u>Vessel wall:</u><br>Thermal: $10^{12}$-$10^{10}$ | | <u>Irradiation time:</u><br>Reactor vessel, grid support....: Reactor Lifetime<br><br>Fuel assembly parts: 3 – 6 years irradiation time<br><br><u>N content:</u><br>If known, around or less than 0.1 % | | | <u>Origin:</u><br>Claddings, castings, tubes, fuel channels,<br><br><u>Irradiation period:</u><br>3 – 6 years<br><br><u>N content:</u><br>If known, between 10 – 35 ppm | | <u>Coolant air ingress control:</u> Yes<br><br>Coolant pH controller in PWR/VVER: LiOH, KOH, Ammonia, Hydrazine,<br>Waste treatment: Decantation, drying, (cementation)<br><br>$^{14}C$ (measured): Yes but not in all Member states<br><br>$^{14}C$ (specification): Mixed | | | | | Relevant for some reactors<br><br><u>Source material (irradiation time):</u><br>Moderator: 10 - 24<br>Shielding: (plant life)<br>Sleeves (5 – 10 years)<br><br><u>$^{14}C$ source:</u> $^{13}C$ (N to a lesser degree) |

Not very surprising; the neutron fluxes and the material in reactors that may be the sources for $^{14}C$ waste vary. With respect to posing the questions concerning the different source material, some general observations may be summarized as:

- Nitrogen content in;
  - Stainless Steel from reactor vessel, grid support, fuel assembly parts.., with irradiation times from 3 – 6 years for fuel associated material, to reactor lifetime for the parts not planned for being exchanged in course of facility lifetime, based upon the information provided by the workshop participants is found to be typically <0.1 %, in good agreement with broader analysis (CAST D7.16.). But not all participants could provide a nitrogen content of the stainless steel used in the plant and activity calculations to determine the $^{14}C$ content have been performed assuming that steel does not contain nitrogen because the nitrogen was not reported. This results in an underestimated $^{14}C$ content.
  - Zircaloy (fuel castings, claddings & tubes) 0.010 – 0.035 %, in the order of 0.030 – 0.010 % previously noted (CAST D6.2 project report (https://www.projectcast.eu/publications)). But not all participant could provide a nitrogen content for Zircaloy. In case of reprocessing waste, a mixture of Zircaloy neutron irradiated in different countries conditioned in a standardized container is the waste to be disposed. The nitrogen content of the national irradiated Zircaloy is then not relevant.
- Coolant pH controller: LiOH, KOH, but also Ammonia and Hydrazine, i.e. materials are still used that add to the Nitrogen content in the cooling circuit.
- $^{14}C$ source in graphite is reported to originate mainly from $^{13}C$, with Nitrogen only to a lesser degree. The reason is the much higher abundancy of carbon in graphite than nitrogen (and oxygen) impurities. As discussed in (CAST D7.16.), the $^{14}C$ distribution varies with its origin. $^{14}C$ from $^{13}C$ is distributed over the graphite bulk material, whereas $^{14}C$ from $^{14}N$ is found on phase boundaries where the nitrogen contaminants are found, i.e. enclosed in pores or chemisorbed on the graphite phase surfaces.

In summary, the information provided is in line with the state-of-knowledge and there are no hints towards additional features or processes not yet identified and investigated.

# 4 Understanding potential 14C release mechanisms

Potential release mechanisms from the different source materials are described in (CAST D7.16.). The discussions during the workshop confirmed these general findings. No specific suggestions were made with respect to how to proceed in order to improve options for treatment and disposal of the $^{14}C$ containing waste.

The findings may be summarized as (for details, see the report):

Table 2.2: Potential $^{14}C$ release mechanisms from $^{14}C$ source material / radioactive waste.

| No | Source material | Potential $^{14}C$ release mechanisms |
|---|---|---|
| 1 | Irradiated Steel | Due to the homogeneous distribution of $^{14}C$ in irradiated steel, a congruent dissolution with the steel corrosion may be argued for. Under normal conditions, this results in a ten-fold lower relative release from stainless steel than from carbon steel. $^{60}Co$ in solution as a descriptor of bulk steel corrosion may be correct for the primary release process, however, is not useful where cobalt is lost from solution through formation of secondary corrosion phases. Finally, corrosion rates determined for stainless steel need to be interpreted with respect to the intact protective oxide layer of the actual material, versus polished material in experiments where the protective layer is destroyed and needs time into corrosion testing in order to be re-established. |
| 2 | Irradiated Zircaloy | Corrosion takes place by oxidation in combination with hydrogen release. The formation of the zircaloy oxide layer is not only a corrosion process, but it is also associated with this being a protective layer against chemical attack. In principle, one would assume that the zircaloy corrosion rate can be quantified by the associated hydrogen formation. Due to hydrogen uptake by the zircaloy, however, the hydrogen/tritium concentration in solution may underestimate the degree of zircaloy corrosion. |
| 3 | Spent ion-exchange resins | The $^{14}C$ trapped on the organic resin ion exchangers can be organic or inorganic carbon . Inorganic $^{14}C$ can be released as carbon-dioxide over the inorganic carbonate species equilibration, in particular during spent ion exchange resin waste processing and storage. Also, the organic $^{14}C$ species bound with different strength and stability to the ion exchange resins, and thus the fraction remaining as a potential source for disposal will also differ from the original distribution in the reactor coolant.<br>During waste treatment with cementitious materials, also inorganic $^{14}C$ is trapped through the alkaline conditions.<br>In the repository, inorganic carbon can be exchanged by, in particular sulphate ions, with the overall release through exchange will depend on the chemical conditions of theses cementitious, concrete systems. The released inorganic carbon is then, however, expected to be retarded through calcite precipitation, as long as the cementitious chemical conditions prevail, i.e. until the cementitious material has degraded and the chemical components diffused away.<br>Despite the comparably small fraction of organic $^{14}C$ species in the ion exchange resins, safety assessment results in these organic species dominating the $^{14}C$ release into the biosphere. The reasons are that despite retention shown by precipitation of some such organic species, the uncertainties are too large with respect to actual processes, and unhindered diffusion is assumed. Better understanding of retention processes of the organic $^{14}C$ species would result in lower /less conservative) dose. |
| 4 | Irradiated Graphite | The potential release mechanisms are associated with different occurrence of $^{14}C$ in graphite. It is found in three different compartments in graphite, namely (i) in the graphite matrix, i.e. in a graphite crystalline lattice position, (ii) pores in the graphite structure, and (iii) bound to the graphite structure surface. Under disposal conditions, large scale oxidation of graphite, the pre-requisite for $^{14}C$ release from the graphite matrix, is not likely to occur. Partial oxidation can generate access to formerly |

| | | |
|---|---|---|
| | | closed pores and enable release from pore-space bound $^{14}C$. Surface bound $^{14}C$ species are expected to become mobilized upon penetration of water to the disposed graphite material. |

# 5 Wrap-up

For wrap-up there were three questions discussed with a broad approach to the status of the scientific-technical knowledge around $^{14}C$ radioactive waste. The questions were related to the status of the R&D at the end of the CAST project, the nature of the R&D status and key outcomes, and how to go about for the next steps.

## - R&D Status: Divergence or Convergence of Knowledge?

The R&D status was discussed in view of the outcome resulting in “divergence” or “convergence” of knowledge. A frequent justification for R&D is that it is conducted in order to decrease uncertainty. In many cases, however, R&D outcome can give the impression of increasing uncertainty instead. This, of course, is not correct. This impression can be perceived when R&D becomes an eye-opener, progressively creating awareness of knowledge missing. Such knowledge missing refers to processes and related data that was not noticed, documented, i.e. the awareness was not there. Identifying such processes and adding them to the overall understanding can give this false impressing of “increasing uncertainty”.

The first question to the participants thus was whether the R&D status in the field of the CAST project generates divergence of knowledge (progressive awareness of knowledge pending), or convergence of knowledge (progressive resolution through additional knowledge). As expected the outcome is mixed, depending on the individual topic within the overall CAST context.

The general conclusion is that the CAST project has provided new knowledge contributing to convergence of understanding. There are still topics where such convergence will require further investigations and rationalization of the knowledge. At the present status, however, there is the understanding that key mechanisms are understood, or that the key questions are at least identified. There is not the expectation that new knowledge will open up new uncertainties. In particular, it was expressed that after the CAST project, a diversity of values remains, but there are bound limits for consideration of importance. The overall contribution of the project thus has been to improve knowledge in a way that contributes to convergence.

Topics that will benefit from additional understanding mentioned were, amongst other:

- Fate of organic $^{14}C$ species after release from the waste material (which species, how stable and mobile are they in which environments, ..).
- The potential role of microbiology in generating mobile $^{14}C$ species from the waste material in case the waste is not processed with cementitious materials
- Quantification of corrosion over long time-periods and associated change in chemical conditions, including generation of hydrogen and its potential impact.

## - R&D outcome: Comfort or Improvement in Solutions and Concepts.

The second question was addressing the outcome of the R&D, namely if it mainly provided comfort in existing solutions and concepts (consolidation), or also provided improvements with respect to solutions and concepts (innovation). The overall impressions included observations, such as:

- Improving confidence in existing solutions and concepts was more important than introducing new ones. The outcome thus may mainly contribute significantly to optimization in different respects, rather than changing the ways things are done.
- There is the potential for improving practical implementation, however, turning the R&D outcome into achieving practical improvements will not only require time, but also improved involvement and exchange with waste generators.

Given that exchange of information of the knowledge acquired will need time, it was concluded that one would need to come back in one of two years and revisit this question.

## - What next: Verify solutions or solve problems

The third and final question concerned the next steps, addressing the question on how to move ahead, including the impact of different magnitudes of $^{14}C$ waste inventories. There were some observations expressed, including:

- Waste characterization is the key for a future solution
- There is the need for exchange on policy and strategic approach for small inventories
- Joint solutions offer a possibility for small inventories to be managed adequately up and until the waste management end-point, i.e. disposal. Such solutions, however, can be expected to be based on the willingness to take action and mobilize the required financial resources for using solutions and facilities that are on an advanced state.

## Annex I: Information provided by different Member States

The information in the below presentations at the workshop is summarized in Table 2.1. The presentations provide information for the following participating Member States:

I. NL
II. BG
III. FI
IV. HU
V. ES
VI. SI
VII. FR

# CArbon-14 Source Term CAST-workshop

Country: the Netherlands

Organisation: COVRA checked by EPZ (Dutch NPP)

Name presenter: Erika Neeft

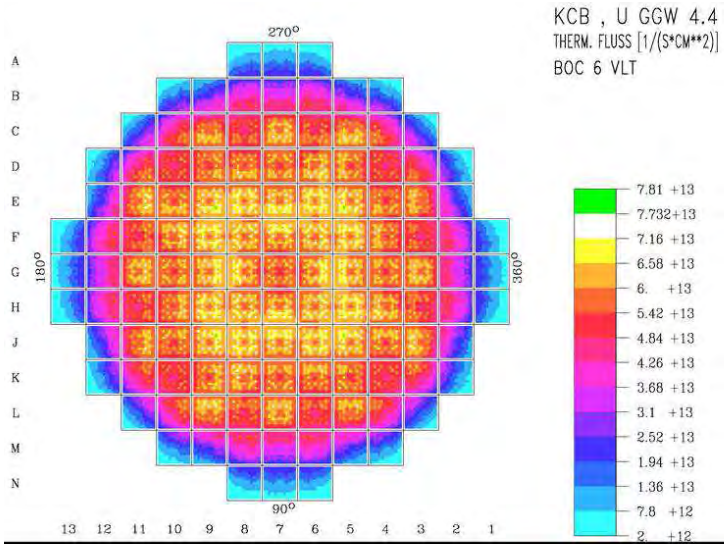
This presentation can/~~cannot~~ be used for the Proceedings of the workshop that will be published at CAST website

**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.**

## What type of reactor

- PWR
  - Gross 515 $MW_e$ ; thermal capacity 1366 $MW_t$
  - Neutron flux (fast, thermal) [neutrons $cm^{-2}s^{-1}$] distribution from core to reflector
  - Inner diameter core 3730 mm

# Example thermal neutron flux in core




# Irradiated Steels

- Expected neutron irradiation period by registration known well, latest delivery to COVRA: 4, 21 and 31 years [c]
- Origin
  - ~~Cladding/~~other (grid support, ducts et cetera)
- Is the nitrogen content of (stainless) steel in the reactor core specified? Yes/No, unknown yet, assumed to be comparable to another Siemens fabricated reactor. For reactor vessel, nitrogen not listed in chemical composition[d]
- If yes
  - Nitrogen content in N ppm or N wt %
    - Vendor specifications or own measurements?

[c] Gesellschaft Nuklear Service documentation
[d] KCB RPV safety assessment assuming 60 years of operation as published by ANVS (Dutch regulator)

# Irradiated Zircaloy

- Limited to claddings
- Zircaloy M5 (PWR)
  - Nitrogen content in ppm
    - Vendor specifications? AREVA Company secret, only public available info – apart from potential CAST reports - Nuclear Engineering International, Manchester Central 24-25 April 2018, nitrogen content **not** mentioned.
  - Neutron irradiation period, not relevant because may not be specific for disposal of Dutch radioactive waste since the spent fuel is reprocessed in la Hague by which the origin of the Zircaloy waste may not be from a Dutch NPP but is expected to resemble French NPP waste. In AREVA specifications carbon-14 content determination, not identified as activation product as e.g. chlorine-36 i.e. Co-60 not a scaling factor

# Spent Ion-exchange resins

- Coolant
  - Is there control of air ingress? Yes, to achieve reducing water chemistry conditions to obtain a sufficient low corrosion potential of 1 ppb $O_2$.
  - Discharged from the plant after cleaning? Yes
- pH coolant controller
  - LiOH for primary coolant (and boric acid). In primary circuit, potential formation of ammonia by dissolved nitrogen and hydrogen is very limited: two weeks after stop: ammonia no longer detected.
  - $NH_2$-$NH_2$ for secondary water circuit [c]
- Waste treatment
  - Fluid with resins ~~bubbled and/or~~ dried ?
    - Further details available for drying i.e. temperature, volume, period of heating evoporator in which waste water is heated.
    - Processed with sludge ;
    - liquid with resin contains about 40 vol% free water, 60 vol% resins of which 55-60 wt% is absorbed water [d]
- Carbon-14 activity concentration measured? ~~Yes/~~No
- Carbon-14 speciation measured? ~~Yes/~~No

[c] IAEA Report of the operational safety review team (OSART) mission to EPZ 9 December 2016 NSNI /OSART/016/178F
[d] EPZ, Waste processing instruction, 2005

# Irradiated Graphite

- Not in EPZ NPP

# CArbon-14 Source Term CAST-workshop

Country: Bulgaria

Organisation: SERAW

Name: Penka Avramova

This presentation can be used for the Proceedings of the workshop that will be published at CAST website

**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.**

# Type of reactor

VVER 440, model V-230

| Unit | Commissioning | Final shutdown | Number of fuel cycles | Generated energy, MWh |
|---|---|---|---|---|
| 1 | 1974 | 31.12.2002 | 23 | 66 675 397 |
| 2 | 1975 | 31.12.2002 | 24 | 68 905 334 |
| 3 | 1980 | 31.12.2006 | 22 | 68 703 260 |
| 4 | 1982 | 31.12.2006 | 21 | 66 711 966 |

## Neutron flux distribution

Neutron flux distribution is estimated according to the report 'Induced activity estimation and dose rate calculation of the equipment and materials in and near reactor core of Units 1 to 4 of Kozloduy NPP', provided by Sofia University under contract № 221000001/13.11.2012

The activation calculations require modeling of neutron transport in the constructive materials outside the reactor core, including distant objects, where neutron flux attenuation is considerably high compared to its values in the core.

Deterministic approach was applied using a modified version of the two-dimensional program DORT in combination with the resources of the program complex SCALE.

Carbon-14 induced activity in the irradiated steels can be determined by applying the methodology and calculation procedure, presented in the report with an interval of 5 years for 100 years period.

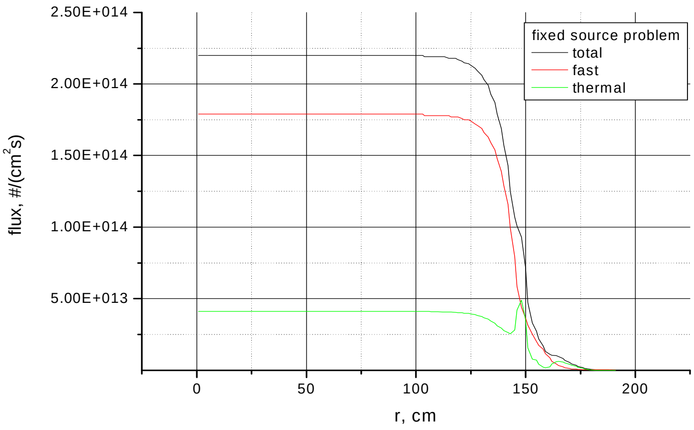
## Neutron flux radial distribution, based on cylindrical model of the core level

Table 2. Material characteristics

<table>
<tr><th></th><th>fuel</th><th colspan="2">cladding</th><th colspan="2">water</th><th>basket</th><th colspan="2">water</th><th>shaft</th><th colspan="2">water</th><th>vessel</th></tr>
<tr><td>zone</td><td>1</td><td colspan="2">2</td><td colspan="2">3</td><td>4</td><td colspan="2">5</td><td>6</td><td colspan="2">7</td><td>8</td></tr>
<tr><td>R</td><td>144. 185</td><td>Thick. 8 mm</td><td>145.27 2</td><td>0.48 g/kg B</td><td>150.5</td><td>154.0</td><td>0.48 g/kg B</td><td>155.5</td><td>161.5</td><td>0.48 g/kg B</td><td>178.0</td><td>192.0</td></tr>
<tr><td>mate rial</td><td>h</td><td colspan="2">5</td><td colspan="2">11</td><td>5</td><td colspan="2">11</td><td>5</td><td colspan="2">11</td><td>6</td></tr>
<tr><td></td><td>air</td><td colspan="2">st3</td><td colspan="2">insulation</td><td>st3</td><td colspan="2">water</td><td>st3</td><td colspan="2">concrete</td><td></td></tr>
<tr><td>zone</td><td>9</td><td colspan="2">10</td><td colspan="2">11</td><td>12</td><td colspan="2">13</td><td>14</td><td colspan="2">15</td><td></td></tr>
<tr><td>R</td><td>196.8</td><td></td><td>197.3</td><td colspan="2">207.0</td><td>209.5</td><td>0.35 g/kg B</td><td>302.5</td><td>305.0</td><td colspan="2">605.0</td><td></td></tr>
<tr><td>mate rial</td><td>12</td><td colspan="2">9</td><td colspan="2">7</td><td>9</td><td colspan="2">10</td><td>9</td><td colspan="2">8</td><td></td></tr>
</table>

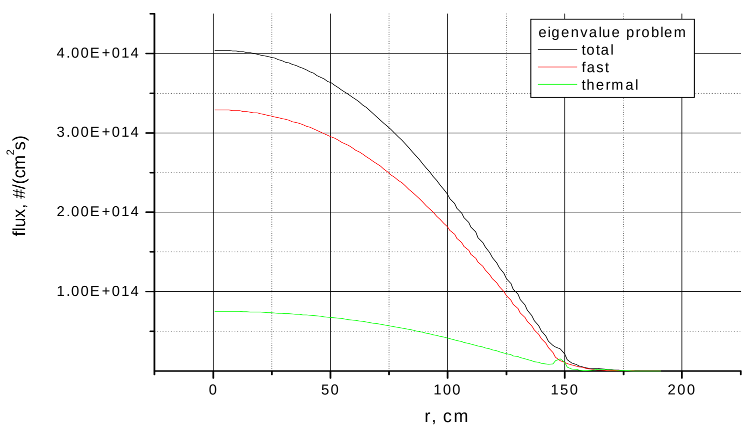
## Neutron flux radial distribution, based on cylindrical model of the core level

Figure 1. Neutron flax radial distribution to the reactor vessel external radius, defined with fixed source



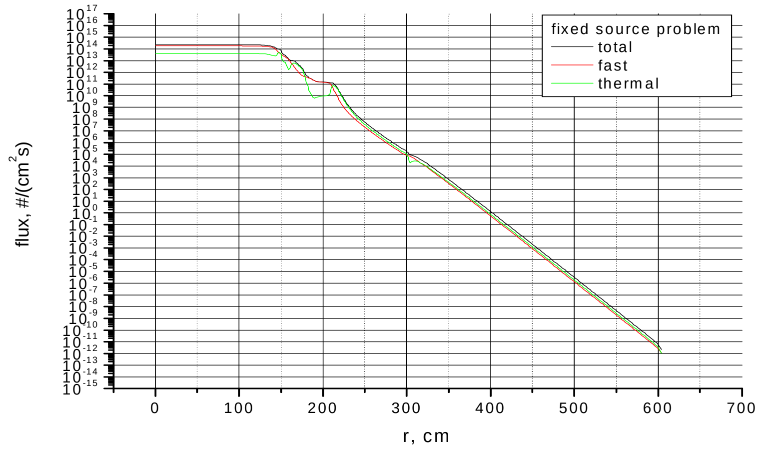

## Neutron flux radial distribution, based on cylindrical model of the core level

Figure 2. Neutron flax to the reactor vessel external radius, defined with eigenvalue



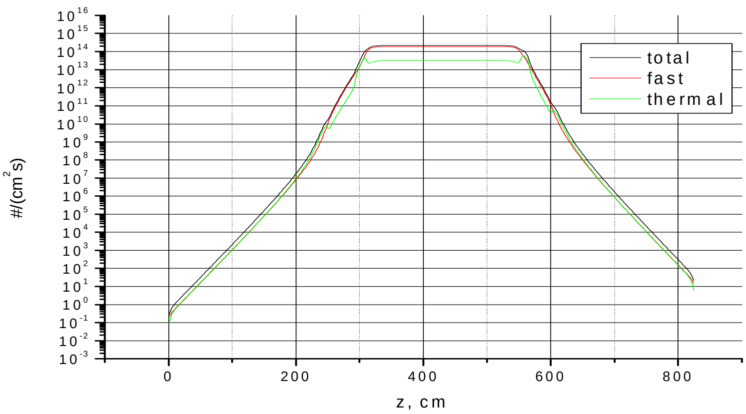
# Neutron flux radial distribution, based on cylindrical model of the core level

Figure 3. Neutron flax radial distribution, defined with fixed source




# Neutron flux axial distribution

Figure 4. Neutron flax axial distribution, defined with fixed source



# Irradiated Steels

- Expected neutron irradiation period
- The load factor during the operational life of the Unit 4 was the 87% and it was operated 21 fuel cycles.
- Typical degree of spent fuel burning was 28.6 MWd/kgU and average enrichment 3.5 % in weight of $^{235}U$.
- The specific induced activity reference date: 01/01/2014.

Table 3. $^{14}C$ values estimated in irradiated carbon steel

| Unit | Min. activity, Bq/g | Max. activity, Bq/g | Activity, Bq | Activity, Bq/g |
|---|---|---|---|---|
| Unit 1 | 1,11E-04 | 1,03E+02 | 5,64E+08 | 1,63E+01 |
| Unit 2 | 1,14E-04 | 1,03E+02 | 5,68E+08 | 1,64E+01 |
| Unit 3 | 7,79E-05 | 7,47E+01 | 4,17E+08 | 1,20E+01 |
| Unit 4 | 1,32E-04 | 1,27E+02 | 7,14E+08 | 2,06E+01 |

# Irradiated Steels

- Origin
  - Cladding, grid support, shaft, basket, ducts, etc.
- Is the nitrogen content of (stainless) steel in the reactor core specified? No

# Irradiated Zircaloy

- Limited to claddings
  - Zirconium alloy, type E110 (99 % Zirconium + 1 % Niobium), is used in the cladding of the fuel assemblies of Russian reactors VVER 440.
  - According to a framework trade agreement between Bulgaria and Russian federation, Spent Fuel (SF) is shipped for reprocessing to Russia, and after that Bulgaria will receive the resulting HLW.
  - These HLW will not contain Zirconium alloys.
  - Nitrogen content in ppm
    - Vendor specifications? No

# Spent Ion-exchange resins

- Coolant
  - Is there control of air ingress? Yes
  - Discharged from the plant after cleaning? No
- pH coolant controller
  - $KOH$ / $NH_4OH$
- Waste treatment
  - Fluid with resins: bubbled
- Carbon-14 activity concentration measured? Yes

  Radiochemical analyses include Liquid Scintillation Counting (LSC) after combustion with oxygen.
- Carbon-14 speciation measured? No

# Irradiated Graphite

Reactors VVER do not use graphite moderators and thus SERAW does not have such kind of RAW.

Thank you for your attention

# CArbon-14 Source Term CAST-workshop

Country: Finland

Organisation: Fortum

Name: Olli Nummi

This presentation can be used for the Proceedings of the workshop that will be published at CAST website

**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.**

## What type of reactor

- VVER
  - 500 $MW_e$
  - Westcott neutron flux [$10^{13}$ neutrons $cm^{-2}s^{-1}$] (core average)

## Irradiated Steels

- Expected neutron irradiation period
  - Total operating time assumed: 50 years
  - Some components are replaced resulting in shorter irradiation times
- Origin
  - Shield elements, reactor pressure vessels, grid support
- Is the nitrogen content of (stainless) steel in the reactor core specified? Yes
- If yes
  - Nitrogen content 0.04 - 0.14 %
  - Vendor specifications

## Irradiated Zircaloy

- Limited to claddings
- VVER
  - Nitrogen content assumption 10-30 ppm
  - Neutron irradiation period 3-4 years

## Spent Ion-exchange resins

- Coolant
  - Is there control of air ingress? Likely yes
  - Discharged from the plant after cleaning? Yes
- pH coolant controller
  - Boron / Ammonia
- Waste treatment
  - Fluid with resins solidified with cement cast into concrete containers
- Carbon-14 activity concentration measured? Yes
- Carbon-14 speciation measured? Yes
- If yes, how?
  - Combustion and acidic dissolution

## Irradiated Graphite

- No graphite produced

# CArbon-14 Source Term CAST-workshop

Country: Hungary

Organisation: Paks NPP

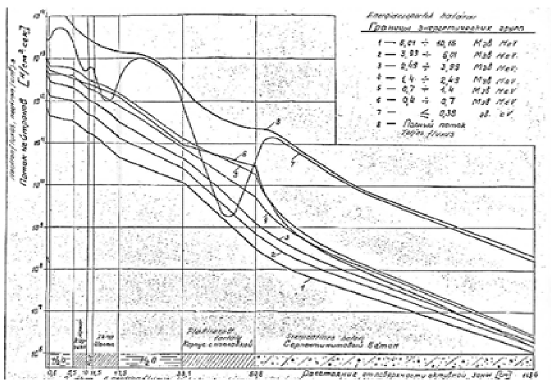
Name: Árpád Nényei, Imre Nemes

This presentation can be used for the Proceedings of the workshop that will be published at CAST website

**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.**

## What type of reactor

- PWR/BWR/**VVER**/RBMK
  - **4 reactor blocks, each of them 500 $MW_e$**
  - Neutron flux (fast, thermal) [neutrons $cm^{-2}s^{-1}$] distribution from core to reflector



# Irradiated Steels

- Expected neutron irradiation period
- Origin
  - Cladding/other (grid support, ducts et cetera)
- Is the nitrogen content of (stainless) steel in the reactor core specified? **Yes**
- If yes
  - Nitrogen content in N ppm or N wt % **0.05 wt%**
    - Vendor specifications or own measurements? **Both (determined in a few samples)**

# Irradiated Zircaloy

- Limited to claddings
- Zircaloy-4 (PWR) / Zircaloy-2 (BWR) / **Zr- 1%Nb E-110 (VVER)**
  - Nitrogen content in ppm
    - **Max. 0.06 wt%**
  - Neutron irradiation period – **4 × 15 months**

# Spent Ion-exchange resins

- Coolant
  - Is there control of air ingress? **Yes**
  - Discharged from the plant after cleaning? **No**
- pH coolant controller
  - **Hydrazine $NH_2$-$NH_2$**
  - Other please specify
- Waste treatment
  - Fluid with resins bubbled and/or dried ? **No**
    - Further details available for drying i.e. temperature, volume, period of heating
- Carbon-14 activity concentration measured? **Yes**
- Carbon-14 speciation measured? **Yes**
- If yes, how?
  - **Only transport water is measured by chemical separation and LSC. (destruction by $H_2SO_4$ (in $N_2$ gas), $CO_2$ gas absorbtion in $Ba(OH)_2$, repeated destruction by HCl (in $N_2$ gas), $CO_2$ gas absorbtion in NaOH, Liquid Scintillation)**

# Irradiated Graphite

- **Not in the Paks NPP**
- Expected neutron irradiation period
  - Moderator / sleeves
- Is the nitrogen content of graphite in the reactor core specified? Yes/No
- If yes
  - Nitrogen content in N ppm or N wt %
    - Vendor specifications or own measurements

# CArbon-14 Source Term CAST-workshop

Country: SPAIN

Organisation: ENRESA

Name: M. Cuñado, G. Serrano, J.L. Leganés

This presentation can be used for the Proceedings of the workshop that will be published at CAST website

**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.**

## What type of reactor

- PWR/BWR
  - $MW_e$ : ~ 1000 current. 160 $Mw_e$ José Cabrera (JC)
  - Neutron flux (thermal) [neutrons·cm$^{-2}$·s-1] (JC)

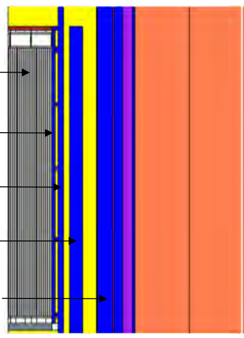
$4 \cdot 10^{13}$ Core

$4.1 \cdot 10^{12}$ Baffle

$2.1 \cdot 10^{12}$ Core barrel

$2 \cdot 10^{11}$ Shielding

$4.9 \cdot 10^{9}$ Vessel wall



# Irradiated Steels

- Expected neutron irradiation period
  - Vessel, internal components, ...: 455 months
    (aprox. 40 years minus 25 refuelling outages of 1 month)
  - Fuel elements: 4 to 6 years
- Origin
  - Main activated components of fuel elements:
    - PWR=>Top nozzle, plenum spring
    - BWR=>Top nozzle, plenum spring, expansion spring

# Irradiated Steels

- Is the nitrogen content of (stainless) steel in the reactor core specified? Yes
- Nitrogen content in N ppm:
  - Vendor specifications SS-304 => 1000 ppm
    Carbon Steel => 84 ppm

# Irradiated Zircaloy

- Limited to claddings and some components in the active region of fuel element (grids and guide tubes in PWR. Grids and fuel channels in BWR)
- Zircaloy-4 (PWR) / Zircaloy-2 (BWR)
  - Nitrogen content in ppm
    - Regulatory limits => 80 ppm
  - Neutron irradiation period
    - PWR 17x17: 3 or 4 cycles x 1.5 years/cycle = 4.5 - 6 y
    - PWR 16x16: 4 or 5 cycles x 1 year/cycle = 4 - 5 y
    - BWR : 3 cycles x 2 years/cycle = 6 y

# Spent Ion-exchange resins

- Coolant
  - Is there control of air ingress? No information
  - Discharged from the plant after cleaning? No information
- pH coolant controller
  - Probably LiOH for PWR
- Waste treatment
  - Fluid with resins bubbled and/or dried ? Decantation
- Carbon-14 activity concentration measured? Yes
- Carbon-14 speciation measured? No
- If yes, how?
  - Combustion with oxygen and liquid scintillation ($^{14}$C and $^{3}$H)

# Irradiated Graphite

- Vandellós I: Graphite Gas Cooled Reactor
- Expected neutron irradiation period
  - Moderator: power plant life => 17 years
  - Sleeves: fuel life
- Is the nitrogen content of graphite in the reactor core specified? No
- Reactor high T and oxidant atmosphere $CO_2$ =>

  $^{14-}$C from N impurities is bound to pores and released during operation.

  $^{14-}$C comes from $^{13-}$C, bound to the crystalline structure. Content linked to the natural relative abundance (1.1%)

# CArbon-14 Source Term CAST-workshop

Country: SLOVENIA

Organisation: Nuklearna Elektrarna Krško

Name: M. Chambers

This presentation can be used for the Proceedings of the workshop that will be published at CAST website

**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.**

## What type of reactor

- PWR
  - 1994 $MW_t$ / 727 $MW_e$
  - Core Average Neutron Flux (3e14 fast, 3e13 thermal) [neutrons $cm^{-2}s^{-1}$]

# Irradiated Steels

- Average neutron irradiation period of 1100 days before discharge.
- Origin
  - Fuel Assembly components
- Nitrogen content of (stainless) steel in the reactor core
  - Stainless Steel 304, 0.1 wt% maximum

# Irradiated Zircaloy

- Limited to claddings
- Zircaloy-4 / Zirlo / Inconel-718 (PWR)
  - Nitrogen content thought to be less than 40 ppm
  - Average Neutron irradiation period of 1100 days.

# Spent Ion-exchange resins

- Coolant
  - Is there control of air ingress? Yes
  - Discharged from the plant after cleaning? Yes
- pH coolant controller - LiOH
- Carbon-14 activity concentration measured? No
- Carbon-14 speciation measured? No

# Irradiated Graphite

- None

# CArbon-14 Source Term CAST-workshop

Country: France

Organisation: Andra

Name:

This presentation can be used for the Proceedings of the workshop that will be published at CAST website

**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.**

# Irradiated Zircaloy

- Claddings
- PWR:Zircaloy-4, M5$^{TM}$, Zirlo
- BWR: Zircaloy-2
- Nitrogen content in ppm

| | Specified or vendors values | | Actual values derived from analysis of castings or tubes | |
|---|---|---|---|---|
| | Zircaloy-4 | M5$^{TM}$ | Zircaloy-4 | M5$^{TM}$ |
| N | < 80 | < 80 | $34 \pm 10$ | $27 \pm 4$ |

# Irradiated Graphite

- Graphite used as neutron moderator
  - Moderator (10-24 years) / sleeves (5-10 years) / biological shielding
- Coolant gas: $CO_2$ or air, approx. 200°C to 500°C
- Source of carbon-14 in French irradiated graphite: **mainly activation of carbon-13** (and nitrogen to a lesser degree)
- Source of nitrogen:
  - carbonaceous materials used in graphite manufacture;
  - air imprisoned in graphite pores;
  - impurity of the gas coolant;
  - air inflows during reactor maintenance cycles.

# Irradiated Graphite

- Bugey Reactor :