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CAST

Advisory Group Review of WP 3 Final Synthesis Report (D1.11)

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CAST – Project Overview

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

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

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

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

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Advisory Group Review of WP 3 Final Synthesis Report

Executive Summary

One of the tasks of the CAST Advisory Group is to review the final synthesis reports from the different Work Packages. This report represents the review of the final synthesis report from WP 3 on the inventory and release of C-14 from zirconium alloys [NECIB ET AL. 2018] and the supporting final reports of the various WP tasks [BOTTOMLEY ET AL. 2018, BUCUR ET AL. 2017, CAES ET AL. 2017, CARON ET AL. 2017, HERM ET AL. 2017, SAKURAGI 2017, SAKURAGI ET AL. 2018].

Significant progress was made during the CAST project on the inventory and distribution of C-14 in Zr-based wastes and on the rate and speciation of release under simulated waste disposal conditions. Excellent agreement was found between predicted and measured C-14 inventories, partly because the N content of Zircaloy and other cladding alloys is known with some confidence. There is also an improved understanding of the relative amounts of C-14 in the oxide and in the metal itself, which will result in an improved instant-release source term for safety assessment. In terms of the release rate and speciation, there is now an excellent body of experimentally measured long-term corrosion rates under anoxic alkaline conditions. However, whether C-14 is released congruently with the slow anoxic corrosion of the base metal is still not clear.

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1 Introduction

The focus of Work Package 3 was the behaviour of C-14 in zirconium alloys used as cladding. Carbon-14 is present in both the base metal (produced by the activation of N-14 impurities) as well as the ZrO_2 layer (additionally formed from the activation of O-17). The Zr-based waste form may be present as intact cladding surrounding the fuel pellets in spent fuel assemblies, or as crushed or compacted hulls cut from individual fuel rods as part of fuel recycling operations. These two waste forms may behave somewhat differently as the effective surface areas contacting the alkaline pore waters will be different and the fragility of the hydrided Zircaloy and other cladding materials may result in fracturing of the hulls during packaging.

Prior to the CAST project, the state-of-the-art treatment of C-14 from Zr alloys in the safety assessment was based on a combination of an instant release fraction (IRF) and slow congruent release [GRAS 2014]. The IRF was based on the C-14 content of the oxide, with some organizations assuming 20% of the total inventory was rapidly released. It was unclear whether the C-14 would be released congruently with dissolution of the oxide, so that the assumption of instant release was clearly conservative. Carbon-14 in the metal itself was generally considered to be released congruently with corrosion of the alloy, with a conservative corrosion rate of 20 nm/yr adopted by a number of organizations. Although it was understood that the specific activity in the oxide was higher than that in the metal, there was a lack of understanding of the chemical state of the C-14 in both. Upon dissolution, both organic and inorganic species were known to be formed. Coupled with the lack of supporting evidence for long-term congruent release of C-14 from corrosion of the metal, there was also uncertainty regarding the impact of hydrides on the corrosion behaviour and, by inference, on the release of C-14. The cladding was known to be extensively hydrided, with the implication that handling, cutting, and compaction of the hulls could lead to fracturing and an increase in effective surface area.

Four tasks were defined for WP 3, namely:

- Task 3.1 – Current status review of Zircaloy corrosion and C-4 release;

- Task 3.2 –Development of analytical methods for measuring C-14 speciation;
- Task 3.3 –Characterization of C-14 released from irradiated zirconium fuel clad wastes;
- Task 3.4 – Synthesis of experimental data and interpretation.

A total of ten different partners undertook activities in one or more of these tasks (ANDRA, AREVA, CEA, EDF, JRC-ITU, KIT, RATEN-ICN, RWMC, SCK-CEN, and SUBATECH). Here the focus is on the outcomes of Tasks 3.3 (Section 2) and the significance of the new data in terms of the safety assessment and safety case (Section 3).

2 Characterization of C-14 released from irradiated zirconium fuel clad wastes

2.1 *Carbon-14 inventory*

Five CAST partners calculated and/or measured the C-14 inventory in irradiated Zircaloy-2, Zircaloy-4, and M5^{TM} cladding, two of whom (KIT, RATEN-ICN) compared predicted and measured inventories.

Although the N specification for Zr-based cladding typically allows for up to 80 wppm N, the actual content of a range of different cladding alloys is consistently in the range 30-50 wppm N [NECIB ET AL. 2018]. Partly because of this relative certainty of the content of the precursor N-14 species (at least in comparison to the wide variability encountered for steels in the CAST project), excellent agreement was reported by both KIT and RATEN-ICN between predicted and measured inventories. In both cases, the agreement was within the reported error of the calculations/measurements. This agreement is somewhat surprising since the measured inventory presumably included a contribution from the C-14 in the oxide, a significant source of which is activation of O-17 that would not have been accounted for based solely on the N impurity content of the alloy. That excellent agreement was obtained nevertheless perhaps indicates that the O-17 activation route is a minor contributor to the overall production of C-14 or may possibly indicate that a portion of the C-14 produced by the activation of N-14 is released during operation and is compensated for by the contribution from O-17 activation. Regardless, these CAST results suggest that the C-14 inventory of Zr-based wastes can be confidently predicted on the basis of activation calculations.

RWMC made separate measurements of the C-14 inventory in the metal and in the oxide, the latter having been removed from the substrate by mechanically crushing the cladding [SAKURAGI 2017]. The specific C-14 content of the oxide is approximately twice that of the underlying metal. Based on the relative dimensions of the oxide and metal, RWMC were able to arrive at a revised distribution of C-14 in the oxide, amounting to 7.5% of the total inventory.

It is interesting to note that despite the differences in N content (17-50 wppm) and burnups (7.5-60 GWd/t_{HM}), the reported (both calculated and measured) C-14 inventories were in the range 1-4 x 10^4 Bq/g. This is a relatively narrow range for safety assessment purposes and suggests that the C-14 inventory for Zr alloys can be defined with some confidence.

Although the speciation of C-14 released during the acid digestion of samples was reported, it is not clear that this speciation would reflect that for C-14 released under anoxic alkaline disposal conditions.

2.2 Speciation of released C-14

Of more interest is the speciation of C-14 released during exposure of irradiated samples to either NaOH or $Ca(OH)_2$ solutions used to simulate the alkaline conditions present in a cemented waste form. The CAST project developed new and important information on the speciation of released C-14, although the issue is clearly complex and incompletely understood. Varied and sometimes inconsistent observations were reported by the three CAST partners involved (CEA, RATEN-ICN, and RWMC), including:

- Only one of the three partners reported gaseous C-14 release, although this may have been because the other two did not attempt to measure it.
- The inorganic/organic fractionation of dissolved C-14 depends on the alloy type (Zircaloy-4 vs. M5^{TM}).
- For Zircaloy-4, one partner reported predominantly inorganic C-14, while another reported a 60:40 organic:inorganic distribution.
- For Zircaloy-2 without the oxide, the gaseous C-14 release fraction decreases with exposure time and the organic:inorganic ratio of the dissolved species increases. Thus, even over laboratory timescales, the speciation is not constant.
- Detailed analysis of the dissolved species was difficult, in part due to the low concentrations involved, and various analytical difficulties were encountered. However, there is evidence for acetate, formate, methane, ethene, and possibly larger carboxylic acids.

The most detailed speciation studies were reported by RWMC (Figure 1). Studies were conducted with and without the oxide attached, the latter presumably designed to represent the long-term release behaviour in the absence of the instant release fraction from the oxide. As noted above, the gaseous release fraction from the substrate decreased with time over the 6.5 year exposure, with the inorganic:organic ratio of the dissolved species also seemingly changing over time. As well as being interesting in terms of defining the speciation for the safety assessment source term, this time-dependent behaviour also calls into question the presumption of congruent release of C-14 from the base metal.

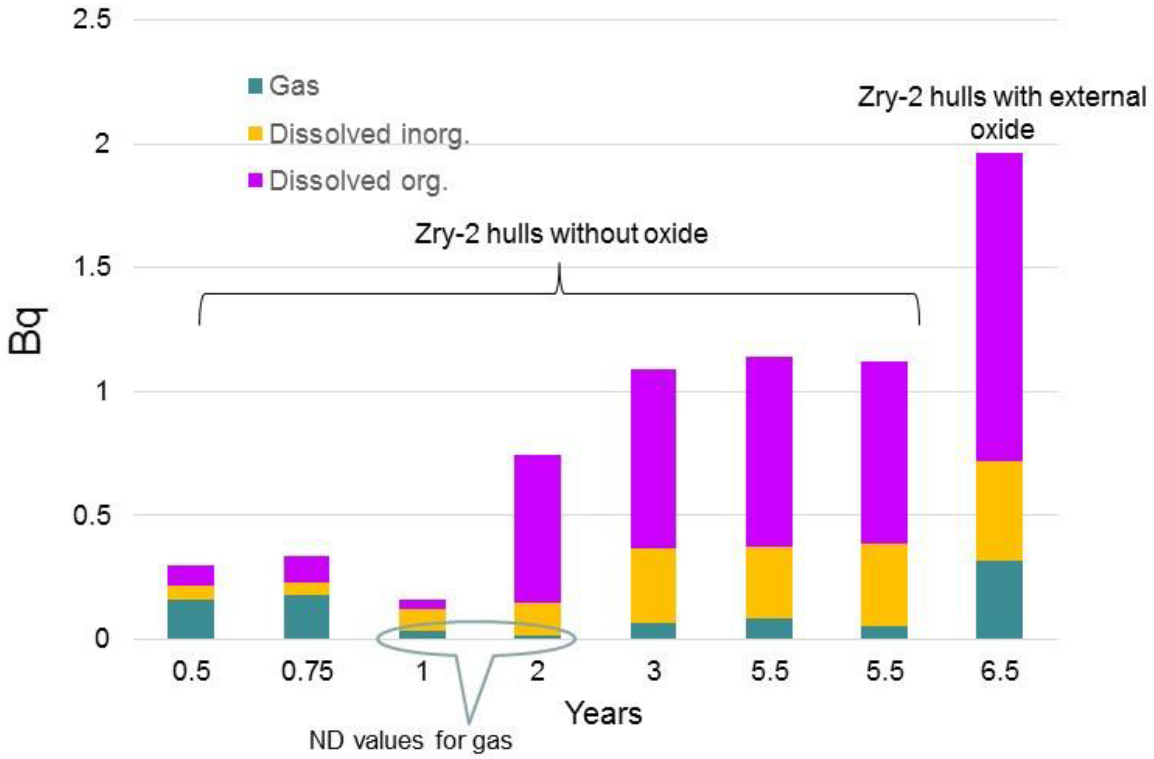

Figure 1: Speciation of C-14 released from Zircaloy-2 during anoxic leaching in pH 12.5 NaOH solution [SAKURAGI 2017]. ND values for gas indicates values were below the detection limit.

2.3 *Corrosion rate measurements*

Various corrosion rate measurements on irradiated and unirradiated Zr alloys in anoxic alkaline conditions were made by three of the partners during the CAST project. Rates were determined using both electrochemical techniques and based on the amount of either evolved H_2 or released C-14. Figure 2 shows the results from RWMC based on the hydrogen production for unirradiated samples or C-14 release for irradiated material (based on the assumption of congruent release). These studies, which were begun prior to the CAST project, represent an excellent dataset with which to predict the long-term behaviour in the repository. In common with nearly all corroding systems, the corrosion rate was observed to decrease with time due to the growth of a thickening passive oxide film. This time dependence was also reflected in shorter experiments commissioned and conducted within the CAST project itself. These shorter tests (limited to a maximum of 18 months exposure) inevitably gave corrosion rates higher than the long-term rates shown in Figure 2.

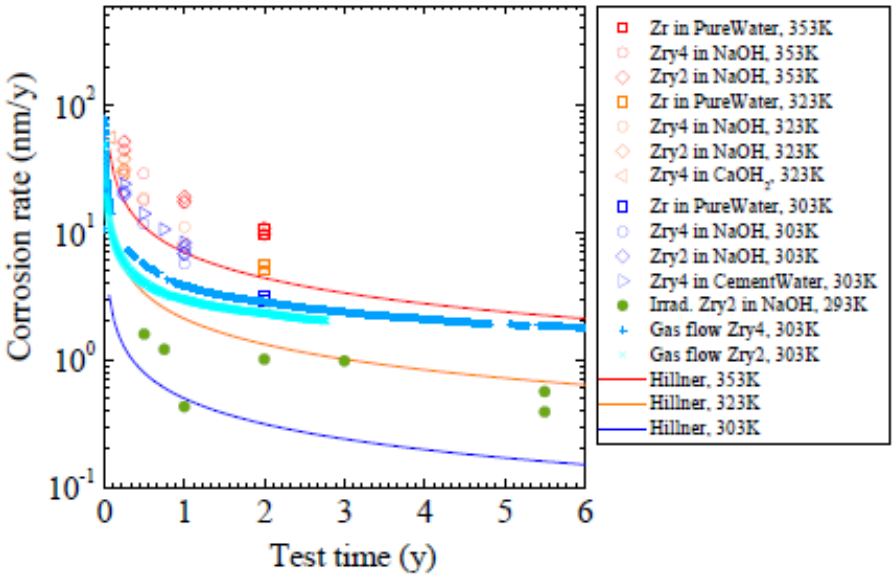

Figure 2: Time dependence of the corrosion rate of irradiated and unirradiated Zircaloy in anoxic alkaline environments [SAKURAGI 2017].

An important question is whether C-14 is released congruently during anoxic corrosion of the metal substrate. For this to be the case, the released C-14 would have to be uniformly distributed within the metal and not retarded by precipitation or incorporation into the growing oxide film. Whether this is the case still remains to be answered and evidence produced during the CAST project is somewhat contradictory. RWMC estimated the corrosion rate of irradiated Zircaloy-2 based on the release of C-14 and the assumption of congruent release (Figure 2). On this basis, the corrosion rate is up to one order of magnitude lower than for unirradiated material under the same conditions. This could be the case as it could be argued that irradiation in-reactor has annealed defects in the film, which could also have been thicker than that on unirradiated material. However, RATEN-ICN, using an electrochemical method, reported a higher corrosion rate for irradiated Zircaloy-4 compared with that of pre-oxidised unirradiated material. Similarly, SCK-CEN reported a high corrosion rate for irradiated Zircaloy-4 (84 nm/yr) based on the rate of C-14 release and the assumption of congruency, although an equivalent rate for unirradiated material was not provided. Thus, it is not clear whether irradiation leads to an increase in corrosion rate. Equally, it is still unclear whether C-14 is released congruently or not during anoxic corrosion in alkaline solution.

2.4 *IRF*

It is commonly observed that, on corrosion of irradiated zirconium alloys, there is a fraction of the C-14 that is rapidly released, followed by slower release of the remainder of the inventory. Historically, it has been assumed that the instant release fraction (IRF) comprises the C-14 inventory of the oxide and that, for safety assessment, it is instantly released. Data from the CAST project suggest that this assumption is highly conservative, as is the previously assumed IRF of 20% of the inventory.

As described above, measurements by RWMC of the C-14 inventory of ZrO_2 mechanically removed from the cladding suggests that the fractional inventory in the oxide is closer to 7.5% rather than 20% [SAKURAGI 2017]. Furthermore, when an oxide-covered sample was exposed to an alkaline leachate, only 0.0038% of the total inventory was released after 6.5 years. If we assume a constant release rate and that all of the C-14 came from the oxide,

it would take 12,800 years (or over two half-lives of C-14) to release all of the oxide inventory. This can hardly be considered to constitute "instant release".

3 Significance of the Outcomes of Work Package 3

Given that the starting point for the treatment of the C-14 source term for zirconium alloys in safety assessments was the presumption of a 20% instant release fraction followed by slow congruent release, significant progress has been made during the CAST project.

We now have a better understanding of the distribution of C-14 between the oxide and base metal and the rate of rapid release, previously considered to be "instant". There is probably sufficient evidence, as well as confidence in that evidence, to reduce the oxide fractional inventory from the earlier value of 20% to something less than 10%. There is also evidence that this fraction is not released instantly, but whether this evidence is sufficient to no longer treat this fraction as "instantly" released is a matter for individual organizations to decide.

There is also consistency, and therefore robustness, in the estimation of the total inventory. Despite differences in N contents, the degree of burnup, etc., the measured and predicted C-14 inventory is within the range 1 to 4 x 10^4 Bq/g, a range that is probably inconsequential in terms of safety assessment.

There are also some areas of continued uncertainty or that have not been addressed in detail, including:

- Is the long-term release of C-14 congruent with corrosion of the Zr alloy substrate?
- Is the corrosion rate of irradiated cladding the same as unirradiated material?
- Can we take credit for the slow release of C-14 from the oxide?
- What is the precise speciation of C-14 released during leaching in anoxic alkaline solution and why does it apparently change with time?
- Is the behaviour of compacted (hydrided) hulls different from that of intact Zr alloy cladding?

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