CArbon-14 Source Term

CAST

Advisory Group Review of WP 6 Final Synthesis Report (D1.14)

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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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(D1.14)

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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 6 on the integration of the CAST results into the safety case and safety assessment [CAPOUET ET AL. 2018].

A number of different aspects of the safety case and safety assessment have been improved as a result of the CAST project. There is improved qualitative understanding of the characteristics of the four different C-14 containing waste forms and their respective leaching behaviour. This mechanistic insight is useful for developing a robust safety case. In terms of quantitative data for use in the safety assessment, progress has been made in quantifying the inventory and/or speciation of released C-14, as well as the release rates. Areas of continued uncertainty are also discussed.

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1 Introduction

The focus of Work Package 6 was the integration of the results from the experimental CAST WPs (WP2-5) into the safety case and safety assessment. In this sense, WP 6 was the "customer" for the output from the other WPs.

Prior to the CAST project, C-14 was handled in the safety assessment in a conservative fashion because of the limited amount of information regarding inventories, release rates, and speciation. However, it was well understood that an understanding of the speciation of released C-14 was crucial to the outcome of the safety assessment due to the different transport and retardation mechanisms. Thus, whilst inorganic C-14 (a shorthand for the carbonate or bicarbonate anion) was understood to the sorbed or retarded by reaction with host minerals and/or cementitious materials, the transport of organic C-14 was not similarly delayed. Compounding the lack of retardation of organic C-14 was the possibility of advective transport of gaseous C-14 (for example, as CH_4) in repository systems in which large volumes of gas may be produced.

Three tasks were defined for WP 6, namely:

- Task 6.1 – Handling of C-14 in current safety assessments;
- Task 6.2 –Knowledge base contextualisation in light of SA hypothesis;
- Task 6.3 –Integration of the CAST results to SA.

Although the emphasis above is on the safety assessment (i.e., the calculation of the radiological consequence of C-14), the CAST results also contribute to the safety case (i.e., the supporting mechanistic understanding and other background information).

A total of fourteen different partners undertook activities in one or more of these tasks (RWM,[1] NAGRA, ANDRA, NIRAS, RAP, GRS, ENEA, RWMC, ENRESA, Fortum, LEI,

[1] Radioactive Waste Management Ltd, the UK organisation responsible for implementing the UK Geological Disposal Facility, was created in 2014. Previously, work now carried out by RWM was carried out by NDA RWMD, the Nuclear Decommissioning Authority Radioactive Waste Management Directorate. The NDA RWMD role in CAST at the project's commencement ceded to RWM in 2014.

NRG, RAWRA/SURAO and SKB). Here the main focus is on the summary report produced for Task 6.3. Detailed safety assessments were conducted as part of the CAST project by a number of partners and the results of these are discussed in detail in HENOCQ ET AL. [2018]. The results from these assessments from the different national programmes are not discussed in detail here, but reference has been made to D 6.3 where necessary for the purposes of the current review.

This report follows a similar format to that used by CAPOUET ET AL. [2018]. First, the contributions from each of the four experimental CAST WPs are reviewed and critiqued in terms of the additional understanding and data for the safety case and safety assessment (Section 2). Next, the implications for the safety assessment are summarised in terms of the three major host-rock types; clay, crystalline, and salt (Section 3). Finally, some additional overall comments are given in Section 4.

2 Improved understanding based on the results from the experimental CAST work packages

2.1 *WP2 steels*

As planned, the results from WP2 contributed new information on (i) the C-14 inventory of irradiated stainless steels, (ii) the release rate, and (iii) the speciation of released C-14.

Reasonable agreement was found between the results of activation calculations and the measured C-14 inventory in stainless steel [MIBUS ET AL. 2018]. Measured and calculated inventories were found to be within a factor of three, although the calculated inventory was lower than the measured. The major sources of uncertainty were stated to be the precursor N content and the precise irradiation history. For safety assessment purposes, a factor of three discrepancy is probably not too consequential, although it would have been preferable if the calculated inventory was higher than the measured value. Nevertheless, with suitable conservatism, the CAST project has demonstrated that activation calculations can provide a reasonable estimate of the inventory as input into the safety assessment.

Historically, the long-term release of C-14 from irradiated steels has been assumed to be congruent with the corrosion of the metal. There was already a good database of measured corrosion rates for stainless and carbon steels in alkaline media prior to CAST. Additional experiments, and the extension of ongoing experiments to longer exposure periods, within the CAST project have built on this database and extended it to include a number of activated samples. Thus, there is a good understanding of the long-term rate of steel corrosion under simulated disposal conditions. The CAST project did not conclusively demonstrate that C-14 is congruently released. Congruent release is a reasonable assumption since, unlike stable C that is primarily present as carbide phases and which may well corrode at different rates from that of the matrix, C-14 may well be uniformly distributed as the precursor N-14 would have been present in solid solution in the original material. However, this remains an assumption which it would be good to validate one way or the other. The CAST experiments on irradiated steels did not provide strong evidence for a significant IRF from the oxide and it seems reasonable to not include a rapid release fraction in the safety assessment.

As noted in the Introduction, improved understanding of the speciation of released C-14 is important for reducing the level of conservatism in the safety assessment. A wide range of C-14 species was observed in leaching experiments with irradiated steels in the CAST project, with both organic and inorganic species in solution and CH_4 and CO in the gas phase. It is difficult, therefore, to closely specify the speciation for future safety assessments. A further complication is the possible role of radiolysis in promoting the release of more-oxidised forms of C-14 [CAPOUET ET AL. 2018], with the implication that the speciation will be time dependent as the gamma field from the irradiated steels decays away.

2.2 WP3 zirconium alloys

As with WP2, the results from WP3 contributed new information on (i) the C-14 inventory of zirconium wastes, (ii) the release rate, and (iii) the speciation of released C-14.

Compared with the situation for irradiated stainless steels, there was excellent agreement between calculated and measured inventories for zirconium wastes [NECIB ET AL. 2018]. Whether this improved agreement was the result of better knowledge regarding the initial N-14 content or the better characterised irradiation history is uncertain, but it is apparent that activation calculations can provide a reliable indication of the total C-14 inventory. There is also improved understanding of the distribution of C-14 between the metal and the oxide, the latter fraction commonly assumed to represent the IRF. It now appears that a better estimate of the oxide fraction may be <10% of the total inventory rather than the 20% previously assumed, although the updated figure is based on a single measurement.

The situation for the long-term release of C-14 from zirconium alloys is similar to that for irradiated stainless steels. Whilst there is an improved database of long-term corrosion rates under simulated repository conditions, there is no definitive evidence of whether the long-term release of C-14 is congruent with corrosion of the metal substrate. However, because the corrosion rate of zirconium is so low in alkaline environments, as is that for stainless steel, the assumption of congruent release is still reasonable in the absence of any obvious mechanism for preferential, accelerated release of C-14 from the metal.

In contrast to the somewhat uncertain situation of release from the metal, there would seem to be a good basis for reducing the conservatism in the IRF based on the improved understanding from the CAST project. Not only may the oxide inventory be a factor of two lower than previously assumed, but only a fraction of that oxide inventory appears to be released rapidly [NECIB ET AL. 2018]. Thus, there appears to be a good basis for reducing the IRF for zirconium alloys in the safety assessment.

As noted by CAPOUET ET AL. [2018], the CAST project has not reduced the uncertainty in the speciation of C-14 released from zirconium alloys. A range of species has been reported [NECIB ET AL. 2018], with both inorganic and small organic molecules in the liquid phase and organic and inorganic gaseous species observed in different experiments.

2.3 *WP4 spent ion-exchange resins*

Perhaps the over-riding conclusion from the WP4 studies on spent ion-exchange resins (SIERs) was that the nature of the waste form is highly variable from national programme to national programme. This makes it difficult, if not impossible, to provide generic guidance or bounding estimates for the C-14 inventory in SIERs. As discussed by REILLER [2018], it will be necessary for each country to carry out a dedicated sampling and analytical campaign to characterise their particular wastes.

Compounding the uncertainty associated with estimating the "initial" C-14 inventory is the fact that a significant fraction may be lost upon drying and treatment of the resins [REILLER 2018]. There are reports that >99% of the inventory is lost upon drying, suggesting that any analytical campaign to characterise the inventory should be conducted on dried resins that will not undergo further treatment prior to disposal.

From a safety assessment point-of-view, the changes upon drying of the resin are important not only for determining the inventory to be disposed but also the associated speciation. The large fraction of C-14 that is lost upon drying is primarily inorganic in the form of CO_2. Thus, the fraction of organic C-14 in the disposed SIERs is higher than would be expected based on the as-received resins from service.

Immobilisation in a cement matrix can also impact the behaviour of C-14 from SIERs. Reaction with the cement strongly retards the release rate, although whether this is significant over assessment timescales is uncertain.

Overall, therefore, although CAST has improved the understanding of the nature and variability of SIERs as a waste form, there still appear to be a number of uncertainties in treating C-14 from this source in the safety assessment.

2.4 *WP5 irradiated graphite*

Unlike the other waste forms considered within CAST, there is considerable variation in the proposed management of irradiated graphite (i-graphite) between the different national programmes. Some countries plan long-term storage, whereas others propose either near-surface or deep geological disposal. The focus in CAPOUET ET AL. [2018] is on the behaviour of C-14 under deep geological disposal conditions with a cementitious backfill.

It is apparent from the results of WP5 that only a fraction of the C-14 in i-graphite is releasable [TOULHOAT ET AL. 2018]. Release is characterised by an IRF followed by a slowly decreasing long-term release rate. The release rate is affected by the pH and redox conditions. The vast majority of the inventory is present as inorganic C-14, but the gaseous release fraction can contain organics (as CH_4). As well as providing improved input data for the safety assessment, the work carried out in CAST WP5 also contributes to improved mechanistic understanding for the safety case.

Partly because of the prior knowledge from the earlier CARBOWASTE project and partly because of separate RWM and LEI programmes on i-graphite, it is possible to define a complete set of input parameters for the speciation and release of C-14 for i-graphite for use in the safety assessment [CAPOUET ET AL. 2018, TOULHOAT ET AL. 2018]. This data set specifically applies to the assessment of C-14 for i-graphite for deep geological disposal in a cementitious repository and CAPOUET ET AL. [2018] caution that the data may not be transferable to other management options. Regardless, the data set comprises best estimates (and, in some, case, upper and lower bounds) for:

- Fractional speciation for dissolved and gaseous C-14 (as either CO or CH_4) for three different combinations of pH and redox conditions (representative of storage in un-grouted containers, early post-disposal in a cementitious backfill, and the long-term repository conditions),
- The fractions of the C-14 inventory that are available for rapid and slower release, and
- The corresponding rapid and slow release rates.

Combined with an estimate for the total inventory, this data set represents exactly the type of input that is needed for the safety assessment. As noted above, that it was possible to produce these data for i-graphite but not for the other waste forms, may be a consequence of the earlier CARBOWASTE and RWM/LEI projects.

3 Significance for the safety case and safety assessment

3.1 *Clay host rock*

Clay host rock provides a robust barrier to the transport of C-14 to the biosphere primarily because of the slow diffusive transport of species. Transit times through the clay barrier can exceed tens of thousands of years, especially for species such as carbonate that react with cement or clay rocks. Thus, speciation of C-14 can be important since organic species are not strongly retarded but if diffusive transport dominates then transit times are still long. Other factors, for example the size of the IRF, tend to have little effect.

One of the few scenarios in which C-14 may be of concern involves advective transport induced by gas build-up and release within the repository. Thus the important factors tend to be associated with the generation and release of gas (such as long-term corrosion rates, how much corrodible metal is present in the repository, and the effective (corroding) surface area), rather than factors associated with the release of the C-14 itself.

3.2 *Crystalline host rock*

Crystalline host rock is characterised by transport along fractures. Thus, the radiological consequences are determined primarily by the ground water flow rate and by the degree of sorption, which in turn is impacted by the speciation.

If transport is (relatively) fast, then the release rate of C-14 would be expected to be important. Thus, it is suggested in CAPOUET ET AL. [2018] that the long-term corrosion rates of steel and Zr and the rate of C-14 release from i-graphite are remaining uncertainties. This suggestion contrasts somewhat with the definition of release rates, releasable fractions, and speciation for i-graphite developed for WP5, albeit these apply strictly only to a cementitious repository. Similarly, it is unclear whether additional experimentation will significantly improve the value for the long-term corrosion rates of steels or Zr, for both of which there is already a data base of long-term rates. Perhaps of more importance would be to demonstrate whether C-14 is released congruently with corrosion of these metals.

It is also suggested in CAPOUET ET AL. [2018] that a remaining uncertainty is the speciation of released C-14 for all waste types. With the possible exception of i-graphite discussed in Section 2.4, it is agreed that there still seems to be significant variation in the nature and relative amounts of organic and inorganic C-14 released from the various waste forms.

3.3 *Salt host rock*

Many of the experimental studies in CAST focussed on anoxic alkaline conditions representative of the long-term environmental conditions in a cement-backfilled repository. These experimental conditions are not representative of those in a salt repository, which somewhat limits the application of the CAST results.

Because of the dry, unsaturated conditions, gas-phase transport dominates in a salt repository so speciation of C-14 (into aqueous and gaseous components) is a key factor. Although some workers addressed this issue in CAST, a number explicitly focussed on either the gaseous fraction or the dissolved fraction. Thus, those concerned with safety assessment of salt repositories are left with some remaining uncertainties, such as:

- What fraction of the C-14 is released in gaseous form?
- How does release vary with time?
- Is the presence of liquid water or humidity necessary to release gaseous C-14?

In terms of the last question, for the corrodible metals at least, the presence of water is required to support corrosion of the underlying metal or to dissolve the oxide. Given that what little water is present is in the form of small brine inclusions, it would seem that there is limited opportunity for corrosion to occur and for C-14 to be released. Whether volatile C-14 can be released from the oxide simply by heating in dry air was not addressed in CAST.

4 Overall comments

One important aspect of the behaviour of C-14 that was specifically excluded from CAST is the impact of the subsequent reactions on the speciation of C-14-bearing species following their release. By design, CAST was specifically focussed on the source term. However, post-release reaction in the near- and far-fields, especially of organics with microbes in the environment, could significantly alter the speciation and transport of C-14. It is accepted that such processes were outside of the scope of CAST, but the possible significance of such reactions should not be overlooked.

There were clearly differences in the quality and quantity of information developed for use in safety assessment for the four different waste forms. For the irradiated metals and SIERs, in particular, there were significant challenges in obtaining active samples and (for the metals) developing sufficiently sensitive analytical techniques. For SIERs there was the additional problem of the wide range in the characteristics of the waste form due to differences in operational history. In contrast, there appears to have been a better existing understanding in the case of i-graphite, which was further built on during the CAST project. Regardless, the CAST project has developed an improved understanding of the behaviour of C-14 for all four waste forms which will improve the overall safety case.

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