

OVERVIEW OF CAST PROJECT

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ABSTRACT. The European Commission CAST project (CArbon-14 Source Term) aimed to develop understanding of the potential release mechanisms of carbon-14 (radiocarbon, ¹⁴C) from radioactive waste materials under conditions relevant to waste packaging and disposal to underground geological disposal facilities. The project focused on the release of carbon-14 as dissolved and gaseous species from irradiated metals (steels, Zircaloys), from spent ion-exchange materials and from irradiated graphites. This paper provides an overview of the CAST project and its output. It also acts as an introduction and scene-setter to the other papers in this special edition of *Radiocarbon*.

KEYWORDS: CAST project, carbon-14, irradiated graphites, irradiated steels and Zircaloys, spent ion exchange resins.

INTRODUCTION

Carbon-14 (radiocarbon, ¹⁴C) is present in important amounts in the radioactive waste inventories of many national waste management programs, particularly in irradiated steels, irradiated Zircaloys, spent ion-exchange materials (resins) and irradiated graphites. The knowledge regarding the chemical form and the release mechanism of carbon-14 from these wastes in disposal conditions—be they surface-based or an underground geological repository—is limited. Conservative treatments are adopted in safety assessments to cope with these uncertainties, possibly giving rise to over-estimated radiological impacts.

The European Commission CAST project (CArbon-14 Source Term) aimed 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 focused on the release of carbon-14 as dissolved and gaseous species from irradiated metals (steels, Zircaloys), from spent ion-exchange materials and from irradiated graphites.

The CAST consortium brought 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 consisted of national waste management organizations, research institutes, universities, and commercial organizations. Although CAST was funded by the European Commission, the participation of non-EC personnel was welcomed.

A number of studies undertaken in CAST or in parallel studies, as presented at the CAST symposium, are reported in this special edition of *Radiocarbon* journal. By source term, these are:

Irradiated Steels

- Release and speciation of ¹⁴C during the corrosion of activated steel in deep geological repositories for the disposal of radioactive waste.

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- ^{14}C release from irradiated stainless steel.
- Carbon-14 release and speciation from carbon steel in highly alkaline conditions.
- Identification of chemical form of stable carbon released from type 304L and 316L stainless-steel powders in alkaline and acidic solutions under low-oxygen conditions.
- Quantification of dissolved organic ^{14}C -containing compounds by accelerator mass spectrometry in a corrosion experiment with irradiated steel.
- ^{14}C release from steels under aerobic conditions.
- ^{14}C release from steels under El Cabril standard leaching test.

Irradiated Zircaloys

- Overview of ^{14}C release from irradiated Zircaloys in geological disposal conditions.
- ^{14}C content in CANDU spent fuel claddings and its release under alkaline conditions.
- Release and speciation of carbon from Zircaloy-4 in anaerobic and highly alkaline conditions: comparison of simple immersion and potentiostatic corrosion tests.

Spent Ion-Exchange Resins

- ^{14}C content in CANDU spent ion exchange resins and its release under alkaline conditions.
- Morphological study of ionic exchange resins to support the ^{14}C release investigation from radioactive wastes—EURATOM CAST project.

Irradiated Graphites

- ^{14}C release from TRIGA irradiated graphite.
- Release of ^{14}C and ^3H from irradiated graphite of the thermal column of VVR-S reactor to solution phase.
- Preliminary investigation of ^{14}C migration from RBMK-1500 reactor graphite disposed of in a potential geological repository in crystalline rocks in Lithuania.
- Estimation of the inventory of ^{14}C and other key radionuclides in irradiated RBMK-1500 graphite based on limited measurements and full 3D core modeling.
- Investigation of impurities of RBMK graphite by different methods.
- ^{14}C leaching and speciation studies on irradiated graphite from Vandellós I nuclear power plant.
- ^{14}C and other radionuclides in impermeable graphite material waste form long term behavior.

Safety Assessments

- Preliminary analysis of gaseous radiocarbon behavior in a geological repository hosted in salt rock.
- ^{14}C exposure from disposal of radioactive waste compared to ^{14}C exposure from cosmogenic origin.

The interested reader is also directed to the CAST website (www.projectcast.eu), where further project deliverables are publicly accessible.

Carbon-14 shows different behaviors in safety assessment calculations depending on whether it is in inorganic or organic form. As carbonate, carbon-14 shows excellent retention in cementitious and clay environments due to isotopic exchanges, whereas it is an unretarded element, possibly in the gaseous phase, when it is an organic species.

The primary focus of CAST was thus to discriminate experimentally between these two different forms, with possibly a more precise characterisation of the speciation of the carbon-14 bearing compounds released from these wastes investigated in this project.

SUMMARY OF PROJECT OUTPUT

For steel and Zircaloy, exhaustive literature reviews and experimental studies on their corrosion rates were carried out in CAST, to bound the carbon-14 source term.

Steel corrosion rates in alkaline conditions are very low because of the presence of a passivation layer [Swanton et al. 2015 (CAST D2.1); Mibus et al. 2018 (CAST D.2.18)]. Many experimental studies have shown that uniform corrosion rates for carbon steel in anoxic, alkaline conditions are below $0.1 \mu\text{m}/\text{yr}$. Recently, an increasing number of studies indicate upper values in the range of few tens of nm/yr . Uniform corrosion rates for stainless steel are very low. In anoxic, alkaline conditions, recent studies reported measured values below $0.01 \mu\text{m}/\text{yr}$. The corrosion rates of stainless and mild steels are higher in neutral conditions than in alkaline conditions. This might affect the carbon-14 release in a pessimistic scenario where the alkalinity of the near field decreases i.e., because of ageing of the cementitious environment. However, the radiological impact remains limited since the pH decreases significantly only in the long-term when most carbon-14 has decayed. The experimental studies indicate an early, fast release of carbon-14 from steel between a negligible fraction up to a few percent. There is no consensus on how to abstract these observations in safety assessment.

The experimental works conducted on the corrosion of Zircaloy in CAST tends to confirm the data reported in the literature with corrosion rates in the order of a few nm/yr at the most at low temperature, in alkaline or neutral conditions [Gras 2014 (CAST D3.1); Necib et al. 2018 (CAST D3.20)]. CAST allowed progress in the knowledge of the corrosion mechanism of Zircaloy. Should the corrosion regime change in disposal conditions (transition to pseudo-linear kinetics), it is not expected to lead to higher rates. Further, the CAST results on Zircaloy confirm the hypotheses formulated 15 years ago by the Japanese program of a mechanism in which carbon-14 is not released immediately by Zircaloy corrosion but is retained inside the oxide film. Indeed, the total leached fraction of carbon-14 from long-term Japanese experiments of several years on pressurized water reactor (PWR) and boiling water reactor (BWR) cladding samples is less than 0.1%. The carbon-14 released in this experiment seems to originate from the oxide layer [Sakuragi et al. 2018 (CAST Final Symposium)]. These experimental results suggest that the 20% instant release fraction (IRF) used traditionally in safety assessment is over-conservative. Unfortunately, there are not enough data and currently no consensus over the release mechanism of carbon-14 from the oxide layer to abstract these very low fractions in quantitative safety assessments. In addition, the influence of hydrides on the corrosion behavior on the long term in disposal conditions remains uncertain. Lastly, it is to be noted that the review work performed in CAST in relation to the Zircaloy inventory in the claddings reduced the uncertainties on the concentration of the nitrogen impurity [Gras 2014 (CAST D3.1);

Capouet et al. 2017 (CAST D6.2)]. However, uncertainty remains in relation to the carbon-14 inventory in reprocessed waste (vitrified and compacted waste). The assumptions regarding the carry-over fractions of carbon-14 inventory from the different components of the assemblies need to be consolidated. Also, accounting for an accessible carbon-14 in the oxide layer in compacted waste (after acid treatment) is still a matter of debate [Capouet et al. 2017 (CAST D6.2)].

The measurements of carbon-14 speciation released from steel show that both organic and inorganic compounds are present in the liquid phase [Mibus et al. 2018 (CAST D.2.18)]. Methane and minor contributions of CO are found in the gas phase. However, applying this speciation to long-term releases of carbon-14 in disposal conditions is debatable. The oxygenated species measured in experimental conditions might in fact result from the radiolysis induced by the activated materials. It could thus be expected that the carbon-14 speciation will shift to reduced compounds, such as—gaseous—hydrocarbons, when the radiolysis becomes ineffective in the disposal system. Carbon-14 from Zircaloy shows the same behavior in terms of speciation: the liquid phase is shared between inorganic and small oxygenated organic compounds. Methane, ethane, and CO₂ were mainly detected in the gas phase. Precise distribution as an input to safety assessment is still challenging at this stage, nevertheless, it can be concluded that the organic form of carbon-14 released from Zircaloy and steel is present in non-negligible fractions.

Spent ion-exchange resins (SIERs) are a heterogeneous source term. The range of activity of SIERs depends on specific factors such as reactor and circuit type, history of the physico-chemistry in the fluid as well as pre-disposal storage conditions and conditioning processes of the resins. Likewise, carbon-14 speciation is expected to be influenced by these factors. In the case of BWR, more than 90% of carbon-14 was found under the form of inorganic carbon. For PWR, the situation is more contrasted. CANDU reactors seem to induce a major part of inorganic carbon-14, whilst for PWR around 20% of carbon-14 was obtained [Reiller 2018 (CAST D4.9)]. The speciation of the organic fraction suggests formic acid as the main organic form in SIERs. The conditioning matrix of SIERs (epoxy and cement) is assigned a safety function of water ingress limitation and possibly retardation in safety assessment [Capouet et al. 2017 (CAST D6.2)]. Experimental studies brought to light the lability of carbon-14 in—unconditioned—SIERs during predisposal processing: the presence of atmospheric air during storage, temperature increase, transient decrease in the pH upon contact with alkaline solutions as well as drying procedures of the SIERs seems to cause a release of inorganic carbon [Rizzato et al. 2017 (CAST D4.8); Reiller 2018 (CAST D4.9)]. SIERs are a telling example illustrating the strong dependency between predisposal and long-term disposal management strategies.

The study of carbon-14 in irradiated graphite in CAST is, to an extent, a continuation of work undertaken in the preceding European Commission CARBOWASTE project. A certain number of outcomes were highlighted in [Toulhoat et al. 2018 (CAST D5.19)]. First, regarding the release rate, a substantial fraction of the carbon-14 in irradiated graphite is not releasable. Some carbon-14 will initially be released rapidly, and some will be released more slowly at a rate that decreases over time. 99% of the carbon-14 that is released is released in the inorganic form. Carbon-14 can be released to both the gas and aqueous phases. A number of different species, including organic species (e.g., CH₄), CO₂ and CO may exist in the gas phase. For high pH conditions, the proportion released as gaseous carbon dioxide is small in comparison to the fractions released as carbon monoxide and methane. CAST provided a consensual parameterisation of the carbon-14 source term in irradiated graphite as basis for safety

assessment. However, these data should be considered with care as the release rate and speciation of carbon-14 is a function of the graphite type used in different reactors and the disposal concept and conditions.

UPSCALING TO GEOLOGICAL DISPOSAL SYSTEMS

Due to its relatively short half-life (5,730 years), the carbon-14 radiological released from the waste through the host rock is sensitive to the release and migration processes in the disposal system.

Clay-based disposal systems provide an excellent performance regarding carbon-14, provided transport times in the disposal system are of the order of a few tens of thousands of years. The carbon-14 activity releases from the geological barrier (whatever its chemical form) are barely sensitive to the instant release fractions (IRF) up to 20% due to the spreading effect of the diffusive transport [Henocq et al. 2018 (CAST D6.3)]. Sensitivity studies show that, in the present state of knowledge reported by PSI in CAST, the possible uptake capacity of the carbon-14 bearing organic compounds identified in CAST is too weak to influence the carbon-14 transport [Capouet et al. 2017 (CAST D6.2)]. The impact of organic carbon-14 might become more relevant in scenarios where diffusion through the geological barrier is cut short, as could occur for example in the case of a scenario that considers transport of groundwater and dissolved species by advection. The impact of this scenario is very dependent on the uncertainties pertaining to corrosion rates, amount of metals and their specific surfaces. Reducing these uncertainties would make it possible to better estimate the source term of both the hydrogen carrier and carbon-14. Different design strategies can also be applied to limit the impact of both the hydrogen pressurisation and the advective transport of carbon-14 [Henocq et al. 2018 (CAST D6.3)].

Locating the repository caverns in crystalline rocks away from any major fracture zones at a sufficient depth limits the groundwater flow through and in the vicinity of the repository caverns. This provides favorable near-field conditions for the engineered barrier system, limits the radionuclide transport, and isolates the waste from the biosphere. In crystalline rocks, any open fractures can provide pathways for both gas and aqueous transport. The release and migration of carbon-14 in organic gaseous form is expected to occur at a rate comparable to the migration of organic carbon-14 dissolved in groundwater. Sensitivity analyses carried out in CAST of carbon-14 releases from a repository located in a crystalline rock indicate a strong impact of the near field processes, i.e., groundwater flow rates and sorption, on the release rates. Consequently, the transport and retardation properties of the ageing cementitious environment are critical. Radiological impact in crystalline rock is more sensitive to IRF and (potential) low distribution coefficients (assigned to cement and host formation) than in clay. Reducing the uncertainties related to the metal corrosion rate as well as a good knowledge of the cementitious evolution is of primary importance for crystalline systems [Henocq et al. 2018 (CAST D6.3)].

A repository for radioactive waste in a salt formation is characterized by mostly dry conditions. Therefore, radionuclide transport occurs dominantly through the gas phase. The convergence of the backfill starts as soon as the repository is closed. This process can be the driver of an advective transport of gases through the EBS up to the biosphere. A potential release of carbon-14 from the repository in salt depends thus on the amount of gaseous carbon-14 made available in the early few hundreds of years after repository closure, due to corrosion by water brought in inside waste packages alongside the waste itself during the operational period or due to initial canister failure. The experimental conditions of CAST (saturated and alkaline) are not directly

representative of the conditions prevailing in a salt disposal (unsaturated & high saline brines). Water being a limiting factor, the impact in salt is very sensitive to the gaseous IRF. Although conditions are different, the literature (First Nuclides) relevant for salt system is in line with CAST. It shows increasing indications that the gaseous release of accessible carbon-14 from Zircaloy (oxide layer), spent fuel rods and steel are relatively low (1% altogether). The highest priority for salt disposal systems is to reduce the uncertainty on the release behavior of gaseous carbon-14. This is mainly related to three questions: (1) What is the percentage of carbon-14 which can be released in volatile form? (2) What is the temporal distribution of this release? (3) Is water necessary to transfer carbon-14 into a volatile form or does this occur in dry conditions? [Henocq et al. 2018 (CAST D6.3)].

KEY MESSAGES TO SAFETY CASE

In conclusion, the experimental studies of CAST have confirmed the release of a non-negligible fraction of carbon-14 organic compounds from steel, Zircaloy and SIERS in alkaline and anoxic conditions.

Regarding Zircaloy and steels, hydrocarbons, and carbon monoxide were found in the gas phase whereas the aqueous phase contained small oxygenated organic compounds. The mechanism of formation of these organics remains uncertain, in particular the source of oxygen. Although the organic nature of carbon-14 products generated from steel and Zircaloy corrosion has been confirmed, long-term generation of carbon-14 in disposal conditions might give a different picture with respect to its organic speciation and compound distribution. Consequently, conservative treatment still applies in safety assessment regarding specific organic speciation. CAST gave the opportunity to reinforce the understanding of the corrosion mechanisms of these metals, in alkaline, anoxic conditions. As a result, the confidence that these corrosion mechanisms will remain generally unchanged in the long term (within a certain Eh/pH window of the near field) has increased. Also, the interplay of the oxide layer in the carbon-14 release mechanism of Zircaloy is now acknowledged. The literature review carried out in CAST confirms the low corrosion rates for these metals as well as the general trend to even lower rates as observed in more recent studies.

CAST emphasized the heterogeneous character of irradiated graphite and spent ion exchange resins. The relative importance in the safety case of carbon-14 (aqueous) versus carbon-14 (gaseous) for these wastes varies by disposal concept, predisposal activities, and operational conditions. Applying the results determined from few specific samples to broad inventories of waste with various operational and predisposal histories must be done with caution. This generalisation process might bring a certain level of uncertainty to be accounted for in safety case. Safety assessment studies carried out in CAST highlighted the critical influence of the chemical and physical evolution of the cementitious environment on different aspects of the carbon-14 source term (e.g., corrosion rates, carbon-14 release rates), but also on more global aspects pertaining to the confinement properties of a geological disposal (e.g., fate of the hydrogen produced by corrosion, near field hydraulic properties). Carbon-14 in the form of a mobile organic compound will give a more relevant radiological impact than if considered in the inorganic form, and this particularly in rapid transport scenarios. Reducing the uncertainty on carbon-14 speciation shifts the conservatism introduced in safety assessment of carbon-14 release to the corrosion and transport rates.

The results from CAST 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. CAST provided an opportunity for training for early career researchers.

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