CArbon-14 Source Term

CAST

CAST outcomes in the context of the safety case: WP6 Synthesis report (D6.4)

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CAST – Project Overview

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

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

The objectives of the CAST project are to gain new scientific understanding of the rate of 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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CAST outcomes in the context of the safety case: WP6 Synthesis report

Executive Summary

Improved understanding of carbon-14 release from CAST –WP2 to WP5 input to WP6

Carbon-14 is present in important amounts in the inventory of many waste families, and particularly in activated steel, Zircaloy (Zy), graphite and spent ion exchange resins (SIERs). The knowledge regarding the chemical form and the release mechanism of C-14 from these wastes in disposal conditions is limited. Conservative treatments must thus be adopted in safety assessments to cope with these uncertainties, giving rise to overestimated radiological impacts. C-14 shows contrasting behaviours in safety calculations depending on whether it is in inorganic or organic form. As carbonate, C-14 shows excellent retention characteristics in cementitious and clay environments due to isotopic exchanges, whereas it is much more mobile and possibly in gaseous phase as an organic species. The primary focus of CAST was thus to discriminate experimentally between these two different forms and to strive for a more precise characterisation of the speciation of the C-14 bearing compounds released from the wastes investigated in this project.

The measurements of C-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 C-14 speciation will shift to reduced compounds, such as – gaseous – hydrocarbons, when the radiolysis becomes ineffective in the disposal system. C-14 from Zircaloy shows the same behaviour in terms of speciation: The liquid phase is shared between inorganic and small oxygenated organic compounds. Methane, ethene and CO_2 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 C-14 released from Zircaloy and steel is present in non-negligible fractions.

For Zircaloy and steel, exhaustive literature reviews and experimental studies on their corrosion rates were carried out in CAST to bound the C-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 µm/year. Recently, an increasing number of studies indicate upper values in the range of few tens of nm/year. Uniform corrosion rates for stainless steel are very low. In anoxic, alkaline conditions, recent studies reported measured values below 0.01 µm/year. The corrosion rates of stainless and mild steels are higher in neutral conditions than in alkaline conditions. This might affect the C-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 C-14 has decayed. The experimental studies indicate an early, fast release of C-14 from steel between a negligible fraction up to a few percents. 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/year 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 fifteen years ago by the Japanese program of a mechanism in which C-14 is not released immediately by Zircaloy corrosion but is retained inside the oxide film. Indeed, the total leached fraction of C-14 from long-term Japanese experiments of several years on PWR and BWR cladding samples is less than 0.1%. The C-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 C-14 from the oxide layer to abstract these very low fractions in quantitative safety assessments. In addition, the influence of hydrides on the corrosion behaviour on the long term in disposal conditions remains uncertain. Last, let's note the reviewing work performed in CAST over the Zircaloy inventory in the claddings that reduced the uncertainties on the concentration of the nitrogen impurity [GRAS, 2014 (CAST D3.1); CAPOUET *et al.*, 2017 (CAST D6.2)]. However, there remains a certain uncertainty on the C-14 inventory in reprocessed waste (vitrified and compacted waste). The assumptions regarding the carry-over fractions of C-14 inventory from the different components of the assemblies need to be consolidated. Also, accounting for an accessible C-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 study of C-14 in irradiated graphite in CAST lies in the continuity of CARBOWASTE. 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 C-14 released is in the inorganic form. C-14 can be released to both the gas and aqueous phases. A number of different species, including organic species (e.g., CH_4), CO_2 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 C-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 C-14 is function of the graphite type used in different reactors and the disposal concept and conditions.

SIERs is a very heterogeneous source. 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, C-14 speciation is expected to be influenced by these factors. In the case of BWR more than 90% of C-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 C-14, whilst for PWR around 20% of C-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 C-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.

Upscaling to geological disposal systems

Due to its relatively short half-life, the C-14 radiological released from the waste through the host rock is sensitive to the release and migration processes in the disposal system. Clay disposal systems provide an excellent performance regarding C-14, provided transport times in the disposal system are of the order of a few tens of thousands of years. The C-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 C-14 bearing organic compounds identified in CAST is to weak to influence the C-14 transport [CAPOUET *et al.*, 2017 (CAST D6.2)]. The impact of organic C-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 C-14. Different design strategies can also be applied to limit the impact of both the hydrogen pressurisation and the advective transport of C-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 favourable 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 C-14 in organic gaseous form is expected to occur at a rate comparable to the migration of organic C-14 dissolved in groundwater. Sensitivity analyses carried out in CAST of C-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 aging 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 characterised by mostly dry conditions. Therefore, radionuclide transport occurs dominantly though the gas phase. The convergence of the backfill starts as soon as the disposal is closed. This process can be the driver of an advective transport of gases though the EBS up to the biosphere. A potential release of C-14 from the repository in salt depends thus on the amount of gaseous C-14 made available in the early few hundreds of years after disposal closure, due to corrosion by water brought 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 C-14 from both the Zircaloy (oxide layer), the spent fuel rod and the steel are relatively low (1% all together). The highest priority for salt disposal systems is to reduce the uncertainty on the release behaviour of gaseous C-14. This is mainly related to three questions: 1/ What is the percentage of C-14 which can be released in volatile form? 2/ What is the temporal distribution of this release? 3/ Is water necessary to transfer C-14 into 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 C-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 remain uncertain, in particular the source of oxygen. Although the organic nature of C-14 products generated from steel and Zircaloy corrosion has been confirmed, long-term generation of C-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 C-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 ions exchange resins. The relative importance in the safety case of carbon-14 (aqueous) versus carbon-14 (gaseous) for these wastes vary 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 C-14 source term (e.g., corrosion rates, C-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). C-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 C-14 speciation shifts the conservatism introduced in safety assessment of C-14 release to the corrosion and transport rates.

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Part 1 – Improved understanding of carbon-14 release and speciation from CAST – WP2 to WP5 input to WP6

1 Carbon-14 release from steel (Mibus J., Nagra)

1.1 *Introduction*

Carbon-14 is an important radionuclide in the inventory of radioactive waste in many disposal programmes. Knowledge on C-14 release from the waste and its chemical form (speciation) is limited which gives rise to uncertainty or the need for overly conservative assumptions in the treatment in safety assessments. C-14 is formed by the neutron activation of N-14 and other nuclides. The majority is contained in activated metals, mainly Zircaloy or steels. In Work Package (WP) 2 of the CAST project the release of C-14 from activated steels, e.g., from reactor internals or the reactor vessel was studied. The main objective of WP2 was to advance our understanding of C-14 behaviour released upon steel corrosion with view on long-term safety assessments. Most experiments applied alkaline, anaerobic conditions referring to a cement based near field in the geologic repository. Some tests involved neutral and acidic pH values to account for uncertainties in the near field evolution as well as aerobe conditions as present during long interim storage or during the early stage after waste emplacement in the repository. The results of CAST WP2 are summarised in [MIBUS *et al.*, 2018 (CAST D2.18)].

1.2 *Inventory*

The inventory is calculated based on the Nitrogen content of the steel and other metallic materials and the neutron flux during reactor operation that depends on the specific position of the piece. Significant uncertainties exist in both the actual amount of N, which can differ significantly from the nominal amount reported by the manufacturer, and regarding the exact position of the metal in question in the reactor and the estimation of the local flux. Uncertainties in the range of 300-400% have been identified between modelled and measured inventories of irradiated steel samples studied under CAST [HERM *et al.*, 2017 (CAST 2.11); MIBUS *et al.*, 2018 (CAST D.2.18)].

1.3 Corrosion rate

The corrosion rate of carbon and stainless steel under conditions relevant to radioactive waste disposal (cementitious, anoxic) have been reviewed by a number of authors [SMART and HOCH 2010; DIOMIDIS 2014]. Corrosion rates are generally very low for both materials under such conditions (a few nm per year) which makes their accurate measurement challenging. The corrosion rate of stainless steel was further measured during the CAST project in an anoxic, alkaline electrolyte by experiment lasting up to 6.5 years, which confirmed the very low rate (down to 0.4 nm/yr at 30 °C) (see Figure 1.1).

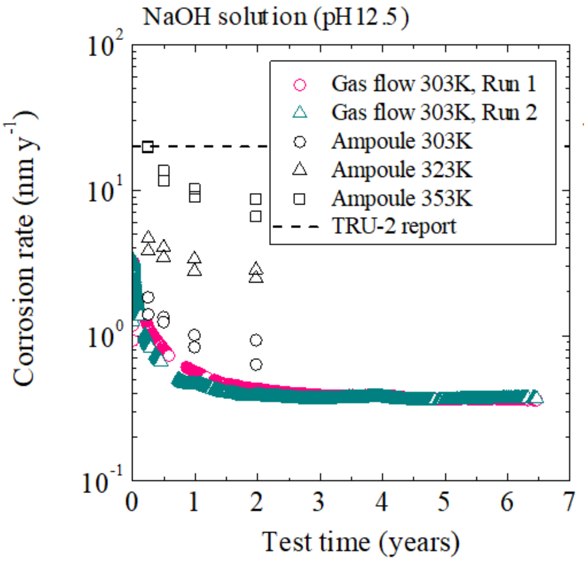

Figure 1.1: Corrosion rate of stainless steel as a function of time and temperature obtained in a dilute NaOH solution of pH 12.5 by the gas flow method and by the glass ampoule method [SAKURAGI, 2017 (CAST2.12)]

Some uncertainty is related to the surface state of the metallic pieces. Surface oxides that were present during operation will tend to be thicker and will have been irradiated, thus O-17 activation may be important and produce C-14 additional to that from N-14 activation. Different surface oxides would be present on metallic surfaces that have been formed by cutting during decommissioning and conditioning of the waste in cement. Oxides would form under oxic unsaturated conditions during interim storage. For carbon steel, corrosion rates in the range of 100 nm/yr are expected under such conditions. We currently have no information on the fate and speciation of C-14 released under interim storage conditions.

1.4 *Release of carbon-14*

1.4.1 Initial release

In the early stage of the leaching experiments, a fast initial release of both C-12 and C-14 to the gas and liquid phase could be observed after immersion of the samples into the leaching solution [DE VISSER *et al.*, 2018 (CAST D2.8 Issue 2); WIELAND AND CVETKOVIĆ, 2018 (CAST D2.19)]. Later, within some days to a few weeks, the release rate decreased significantly. This initial release was dominated by dissolved species, mainly carbonate and carboxylic acids, accompanied by a significantly smaller fraction of gaseous species (CO and methane). Quantitatively, the initially released C-14 made up a fraction between 10^{-6} [DE VISSER *et al.*, 2018 (CAST D2.8 Issue 2)] and 3.6 % [RODRIGUEZ ALCALÁ *et al.*, 2018 (CAST D2.13)] of the total C-14 activity of the metal piece studied. This initial release was attributed to C-14 species encased in the oxide layer formed on the steel and surface contaminations. As the resaturation process in a real repository will take much longer than simulated in the experiments, the observed fast initial release will stretch over a longer time period. Whether this initial release has to be considered as an Initial Release Fraction (IRF) in safety assessments or not, depends on the disposal system, mainly on the transport mechanisms and travel time to the biosphere, and has to be decided on the base of a more detailed analysis.

1.4.2 Long-term release

After the transient at the beginning of the experiments associated with a decreasing release rate as described above, it can be assumed that the C-14 is released upon corrosion of the bulk metal. The later established release rate is low and could be quantified only in very few experiments, e.g., [DE VISSER *et al.*, 2018 (CAST D2.8 Issue 2); WIELAND AND CVETKOVIĆ, 2018 (CAST D2.19)]. In fact, as a first approximation, this C-14 release rate seems to correspond to the corrosion rate of steel. The corrosion rate, however, undergoes rapid changes in the early stage of the experiment (see Figure 1.1 [SAKURAGI, 2017 (CAST 2.12)]). The conclusion of a C-14 release congruent with the steel corrosion is therefore subject to high uncertainty.

1.5 *Speciation*

The measured speciation of C-14 comprises both organic (carboxylic acids) and inorganic compounds (carbonate) in the liquid phase. Methane and minor contributions of CO were found in the gas phase. The major part of C-14 was released to the liquid phase. A systematic shift in speciation between the initial release and the slower release in the later phase of the experiment could not be observed. It can be assumed that initially released species were formed during operation in the reactor and interim storage. The entrapment mechanism in the surface layer is however not clear.

In the experiments, no systematic differences in the behaviour of C-12 and C-14 could be observed. However, no rigorous comparison of the behaviour of both isotopes has been made and it can thus not entirely be excluded that differences exist.

It could be observed that samples featuring a higher dose rate (Wood/NRG [DE VISSER *et al.*, 2018 (CAST D2.8 Issue 2)]) tend to produce more carbonate in the liquid phase and CO in the gas phase. In an experiment using a piece with a lower dose rate (PSI, [WIELAND AND CVETKOVIĆ, 2018 (CAST D2.19)]), the solution was dominated by carboxylic acids and the gas phase by methane. That indicates that the higher dose rate and the presence of oxidants due to radiolysis might influence the speciation of carbon after release from activated steel.

1.6 *Possible long-term evolution*

During the early stages of disposal, exposure conditions will remain relatively unchanged (oxic, unsaturated). The only major difference would be an increase of the relative humidity to 100% relatively soon after sealing of the emplacement cavern. An appreciable effect would be expected in the case of early water ingress, leading to oxic and saturated conditions. Such conditions would be expected in repositories constructed in fractured crystalline rocks. In absence of early water ingress, as would be expected in clay-based repositories, oxic unsaturated conditions are expected to gradually evolve to anoxic unsaturated conditions as oxygen trapped in the cement pore space is consumed by corrosion and other processes.

The released dissolved C-14 species can only slowly diffuse away in the thin water film of the unsaturated cement backfill and accumulate near the metal / cement interface; as soon as phases become supersaturated, they may precipitate. Carbonate forms calcite, oxalate might form calcium oxalate (whewellite) in the calcium rich cement pore water. Gaseous compounds in contrast, may diffuse through the gas filled pore space or even be advectively displaced due to pressure build-up in the gas phase [DIOMIDIS *et al.*, 2016].

Partly saturated conditions may prevail for many thousands of years as water ingress is counterbalanced by gas generation. For example, for a Swiss repository in Opalinus Clay, the cementitious nearfield remains only partly saturated for at least 100 000 yrs [DIOMIDIS *et al.*, 2016]. This is about 17 half-lives, indicating that any C-14 release would be under unsaturated conditions. Upon saturation, corrosion rates are not expected to significantly change and will remain in the range of a few nm per year.

The release of C-14 from activated steel in the early phase, i.e., after the first contact of the metal surface with water, will involve the chemical compounds found in the early stage of the leaching experiments. It can be assumed that mainly oxygen containing species like carbonate or carboxylic acids are released to the liquid phase and some smaller amounts of methane and also CO are transferred to the gas phase.

After release of C-14 compounds from the metal oxide layer, the C-14 from the bulk material will be released upon further steel corrosion. It is still unclear what the source of oxygen for the formation of carbonate or organic compounds with oxygen-containing functional groups will be. From two experiments (see Section 1.5), the conclusion can be drawn that radiolysis with subsequent formation of oxidants may enable the formation of these species. While this may be an explanation for experimental results, it must be considered if this effect may play a role in the real repository. Due to the formation of large amounts of gas, mainly hydrogen due to the corrosion of metallic waste, significantly more oxidants produced by radiolysis would be consumed by dissolved H_2 [PASTINA and LAVERNE, 2001] compared to the experiments where only one piece of metal slowly produced a small amount of H_2. This effect would mean that the speciation under real repository conditions can be expected to shift towards hydrocarbons without oxygen containing functional groups such as methane implying the formation of gaseous species instead of dissolved.

Later, the impact of irradiation and radiolysis on the chemical conditions in solution in the repository will decrease with the decay of relatively short-lived gamma emitters like ^{60}Co. Model calculations in [NAGRA, 2002] consider a time frame of 1000 years to reduce the beta and gamma activity in a Swiss ILW repository by a factor of 100. It can be expected that at the latest then the influence of radiolysis on the formation of oxygen containing C-14 species will be diminished. As a consequence, the formation of gaseous hydrocarbons can be expected to increase during the long-term release.

2 Carbon-14 release from Zircaloy (Necib S. and Schumacher S., Andra)

2.1 *Introduction*

The results presented thereafter come from the work carried out within the Work Package 3 (WP3) on Zircaloys used as cladding materials in nuclear power plants. The objectives of this WP is to bring a better understanding of the release mechanisms of C-14 from irradiated Zircaloys in alkaline media, relevant to disposal conditions.

Various unirradiated and irradiated materials have been investigated: Zircaloy, Zircaloy-2, Zircaloy-4, M5^{TM} corresponding to different types of reactors: BWR, PWR, CANDU… Their history was also different (burn-up, cleaning process…). Consequently, there was a wide range of available materials and conditions to investigate.

2.2 *C-14 inventory*

In the claddings, C-14 comes from the activation of nitrogen (for the metal part) and oxygen 17 (for the oxide part). In CAST, the nitrogen content was determined experimentally (SCK•CEN) and is in the range of 20-30 ppm [CAES *et al.*, 2017 (CAST D3.17)].

The work carried out within the CAST project has shown that modelling allows for accurate assessment of the C-14 inventory of an irradiated Zr-4 cladding. For instance, KIT measured the C-14 inventory on irradiated Zr-4 from irradiated UO_2 fuel rod segment (burnup of 50.4 GWd/tHM). The inventory of C-14 present in irradiated Zircaloy-4 (experimentally determined independently in five specimens) was $3.7 \pm 0.4 \times 10^4$ Bq/g Zr-4 with sufficient reproducibility [HERM *et al.*, 2015 (CAST D3.8); HERM *et al.*, 2017 (CAST D3.15)]. Two modelling approaches were conducted to assess C-14 inventory: (i) The neutron flux of the subassembly was simulated using the Monte Carlo N-particle code (MCNP) and finally the CINDER program calculated the activation of the material [WILSON *et al.*, 2008;

PELOWITZ, 2011], (ii) The SCALE/TRITON package was used to develop cladding macro-cross-section libraries, which were used in the ORIGEN-S program to calculate the radioactive inventory of the cladding [GAULD *et al.*, 2009; ORNL, 2011]. The former gave a C-14 inventory of $3.5 \pm 0.4 \times 10^4$ Bq/g Zr-4 and the latter showed an equivalent C-14 inventory of $3.6 \pm 0.4 \times 10^4$ Bq/g Zr-4. Overall, the results obtained by modelling and experimentally showed similar C-14 inventory for the irradiated Zr-4 studied by KIT.

The same conclusions may be drawn from RATEN ICN [BUCUR *et al.*, 2017 (CAST D3.16)] results: the experimental results are in good agreement with the calculations. In addition, they confirm the data reviewed in the reports [GRAS, 2014 (CAST D3.1)] and [CAPOUET *et al.*, 2017 (CAST D6.2)] report with a C-14 specific activity in the order of $1\text{-}4 \times 10^4$ Bq/g of Zr. At first glance, the results do not seem to show a clear relationship between the burn-up and the C-14 specific activity but it must be kept in mind that the zirconium alloys are not the same (Zr-2, Zr-4, M5^{TM}) and originate from different reactors (CANDU, BWR, PWR).

In most cases, the inventory was determined as the total specific activity in the metal and oxide. Work carried out by RWMC on irradiated Zr-2 showed a concentration twice higher in the oxide than in the metal: about 5×10^4 Bq/g Zr against 2.5×10^4 Bq/g Zr [SAKURAGI, 2018 (CAST D3.19)].

2.3 *Corrosion rate*

GRAS [GRAS, 2014 (CAST D3.1)] reports recent results of Zr-4 corrosion rates of a few nm/y after a few years of corrosion test. These results seem to be confirmed in WP3 [SAKURAGI, 2018 (CAST D3.19)].

- RWMC performed hydrogen measurements for unirradiated Zircaloys. The results show a decrease of the corrosion rate with time starting from 30 nm/yr and reaching about 5 nm/yr after 2 years of exposure in NaOH solution, pH 12.5 at room temperature in anaerobic conditions (Figure 2.1).

- There is a limited influence of pH above neutral: the results of the experiments conducted by RWMC in pure water and cementitious water follow a similar trend. However, the corrosion rate was decreasing more slowly in cementitious water than in NaOH solution and pure water. After two years, the measured values were respectively 8 nm/yr and 2 nm/yr. In addition, these results were significantly different from those obtained by using high temperature post-transitional corrosion rate equation [HILLNER, 1977]. This indicates that the corrosion process at high temperature and low temperature is not strictly the same. This is at odds with Maeda [MAEDA *et al.*, 2014] who confirm that the cubic law for the pre-transitional corrosion rate derived by Hillner [HILLNER *et al.*, 2000] in operational conditions is applicable to low temperature. Nevertheless, the CR seems to slow down with time and it is not expected to have values higher than a few nm/yr in the post-transition regime.

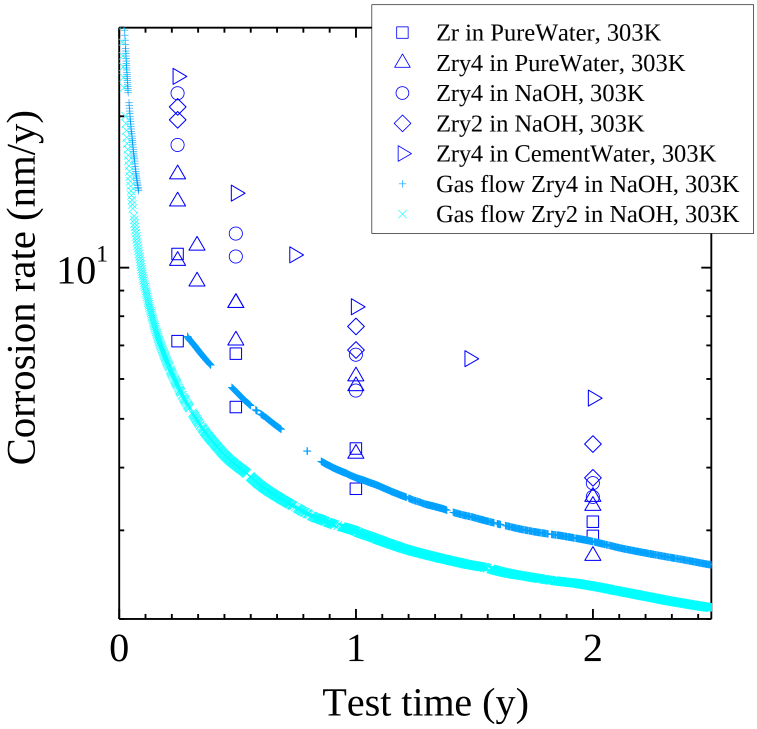

Figure 2.1: Corrosion rate of unirradiated Zr alloys at 303 K

- There is no clear evidence on the effect of irradiation on the corrosion rate. Hillner [HILLNER *et al.*, 2000] reported observations that the effect of irradiation increases the corrosion rate by a factor of 2 or less before 110 days of post-irradiation exposure at

280 °C. The experiment was not conducted for sufficient time to observe convergence with non-irradiated corrosion. These results were supported by the results of RWMC within the CAST project. By contrast, RATEN ICN and SCK•CEN found lower corrosion rates for unirradiated Zircaloys rather than for irradiated Zircaloys, but the techniques used (electrochemical measurements and gas measurements) were different from those of RWMC (based on C-14 measurements for irradiated samples).

- The building up of the oxide layer lowers the corrosion rate (results from RATEN ICN [BUCUR *et al.*, 2017 (CAST D 3.16)] on three types of unirradiated Zr-4 samples: free from oxide, oxidised and cut at one end). Indeed, pre-oxidised Zr-4 samples have a lower CR than the as-received ones. In addition, oxidised samples with fresh surface exposed to solution have a higher corrosion rate than the samples oxidised uniformly on surface (see Table 2.1).

Table 2.1: LPR results obtained for non-irradiated Zy-4 samples at applied potentials of ± 10 mV vs Ecorr [BUCUR et al., 2017 (CAST D 3.16)]

Samples	E_{corr} (V)	i_{corr} (A/cm²)	Corr. rate (mm/y)	Corr. rate (nm/y)	Polarization resistance (Ω)
As received Zy-4 tube	-0.84	1.0E-8	1.1E-04	111	2.4E+5
Oxidised Zy-4 tube	-0.300	2.7E-10	3.1E-06	0,31	1.5E+7
Oxidised Zy-4 tube cut at one end	-0.220	5.5E-9	6.34E-05	63,4	1.7E+5

- Effect of temperature: RWMC experimental program in CAST shows that the effect of temperature on the corrosion rate is less pronounced below 100 °C. The corrosion rate reaches 10 nm/y after 2 years of corrosion at 80 °C. This is in agreement with [HILLNER *et al.*, 2000].

- Effect of the type of cladding: experiments carried out in CAST do not show any evidence of the influence of the type of zirconium alloy (Zr-2, Zr-4, M5^{TM}) regarding the corrosion rate. However, at high temperature, it is well known that the type of Zircaloy has an influence.

- The influence of hydrides on the corrosion rate was not investigated in the CAST project. The tested samples were either hulls or samples from spent fuel. The samples were not compacted as expected for the real waste. Therefore the risk of hydrogen embrittlement for hydride hulls in a compacted stage was not investigated in CAST. In addition, the solubility of hydrogen at low temperature being almost zero, hydrogen embrittlement is unlikely. From the observations made in WP3, there was no evidence of localised corrosion due to hydration.

2.4 *C-14 release*

2.4.1 Instant Release Fraction

As C-14 is located both in the oxide and in the metal, C-14 release in safety assessment corresponds to the sum of the release from the metal, which is often conservatively assumed to be congruent to the corrosion of the metal, and the release from the oxide [1]. In absence of knowledge regarding the C-14 release behaviour in the oxide layer, the fraction of the C-14 inventory located in the part of the material is assumed to be loosely associated to the metal oxide and is realised entirely upon contact with water. The fraction of the inventory corresponding to this instant release fraction (IRF) depends on the thickness of the oxide layer, and the C-14 concentration in this layer comparatively to the C-14 concentration in the metal. The type of zirconium alloy influences also the oxide thickness: it is greater for Zr-4 than for M5^{TM} or Zirlo^{TM}. The most commonly used value in safety assessment for the fraction of Zr-4 inventory in the oxide is 20%. This value is set on the hypothesis of extreme corrosion.

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[1] In the CAST project, only the external oxide has been considered (see RWMC's work). Nevertheless, the internal oxide needs to be taken in consideration as well as it is closer to the fuel and its inventory cannot be neglected.

Indeed, maximum values of 100 µm on a 500 µm thick Zy-4 cladding are only observed locally in the upper part of the rod in PWR conditions. According to [GEBHARDT and GOLL, 2012], the typical corrosion layer thickness of BWR fuel rods remain below 100 µm up to high burnups.

In the CAST project, RWMC [SAKURAGI, 2018 (CAST D3.19)] measured the ratio of C-14 specific activity between the oxide layer and the metal. This ratio was about 2.8 for an irradiated cladding (Zr-2, average rod burnup of 41.6 GWd/t_U) with a 25.3 µm thick external oxide film, which leads to the following C-14 inventory: 92.5 % in the metal and 7.5 % in the oxide. This suggests that the 20 % used in safety assessment are too conservative. However, previous studies carried out on PWR cladding (Zr-4) revealed 17 % for the total C-14 measured in the oxide [YAMAGUCHI *et al.*, 1999], knowing that the oxide was significantly thicker (80 µm).

Recent studies carried out for 6.5 years on Zr-2 samples (free from internal oxide) in NaOH solution showed a very low released fraction of C-14 (about 0.0038 %), coming mainly from the oxide layer. The results were obtained by measuring the total C-14 released in solution over a period of 6.5 years. The ratio C-14 release/C-14 inventory was calculated to be 0.038%, which is negligible and far below the estimated IRF.

Sakuragi *et al.* (2018, CAST Final Symposium) carried out long-term experiments on Zr-4 cladding samples (free from internal oxide) in NaOH solution. The total leached fraction of C-14 from a long-term experiment on PWR cladding samples performed by is less than 0.1% after two years of measurements. Longer experimental studies (up to 6 years) performed on BWR samples do not show an increase of C-14 after that period. Assuming that PWR and BWR have similar behaviors, the early and incongruent release from PWR hulls would be less than 1%. Based on kinetic relationships derived at high temperature in operational conditions, Sakuragi *et al.* (2016) calculate that the C-14 released in this experiment originates almost entirely from the oxide layer. These experimental results tend to confirm the strong conservatism of 20% used traditionally in safety assessment.

Both the low amount of C-14 in the oxide and the low leaching rate indicate that C-14 in the oxide is not significant in terms of instant release fraction; this understanding should be reflected in the safety case. Other mechanisms need to be taken into consideration to explain the C-14 release from the oxide and metal.

Recently, EDF [NECIB *et al.*, 2018 (CAST D3.20)] has launched ab-initio calculations to determine the diffusivity of carbon both in the metal and in the oxide. Migration energy of carbon in zirconium and in zirconia have also been calculated (see Table 2.2). The method is in two steps: the first one is to calculate the migration energies between the various interstitial sites in the metal or in the zirconia and the second one is to incorporate these “local” migration energies in a specific code (LAKIMOKA) to calculate a “global” diffusion coefficient averaged on all the possible diffusion paths correctly weighted. The diffusion coefficient is written according to the classical Arrhenius formalism:

$$D = D_0 e^{E/kT}$$

Where,
D_0 is the pre-exponential coefficient ($m^2.s^{-1}$),
E is the migration energy (eV),
k is the Boltzmann constant ($eV.K^{-1}$),
T is the temperature (K).

Table 2.2: Calculated diffusion coefficients of C in zirconium and in zirconia. Diffusion is considered as interstitial. L is the average diffusion length ($\sqrt{Dt}$ where t is equal to 100 000 years and D is the diffusion coefficient calculated at 50°C).

	D_0 ($m^2.s^{-1}$)	**E (eV)**	**L (µm)**
Zirconium	6.02×10^{-7}	2.02	10^{-6}
Zirconia	1.6×10^{-7}	1.19	0.8

According to the calculated diffusion coefficients, the depth from which the carbon could migrate to the leaching water is very small even after 100 000 years. It means that the most important point to consider is the water penetration in the oxide. As mentioned previously, it is known that the external, post-transition, oxide layer is porous, open to water. Pores of diameter less than 1 nm have been observed [NI *et al.*, 2010] so the oxide is porous but remains very dense. The migration of species in this poral water is not known. Recent calculations have been done to check the possible influence of the surface. In fact the oxide surface induce a modification of the electronic and the lattice structures in its neighbourhood. As a matter of fact, calculations show that carbon diffusion in subsurface is enhanced.

Characterizations by CEA [KASPRZAK *et al.*, 2017 (CAST D3.18)] on the oxide layer of Zr-4 and M5^{TM} hulls using RAMAN spectroscopy observations confirmed that the acidic treatments performed on the hulls did not change the structure of the oxide layer already formed in reactor (ZrO_2 monoclinic structure). In addition, the observations revealed the presence of defects in the oxide layer. The observations performed before and after the leaching experiments were similar. Microcracks were also observed on leached irradiated samples by RATEN ICN (but not on unirradiated samples), suggesting that the cracks could be potential pathways for the transport of dissolved species.

All these studies stress that considering an IRF of 20 % is overconservative.

2.4.2 Speciation

The inorganic / organic partition was determined on liquid samples by using the LSC technique. Most results show that for Zircaloy samples containing both the metal and oxide, the organic fraction is more important than the inorganic one. This is reflected in the results of RWMC (on Zr-2) and RATEN ICN (on CANDU Zr-4) which showed a C-14 partition of 60-70 % organic and 30-40 % inorganic C-14. By contrast, CEA and SUBATECH found that the inorganic form is the predominant one (from 55 %/ 45 % inorganic/organic up to 93 % / 7 %). However, it should be noted that their results reveal discrepancies despite the fact that the analyses were conducted on the same leachates.

Most of the results showed that the ratio between the inorganic form and the organic form does not evolve over time (up to 18 months). RWMC showed that C-14 release at early stage (up to one year) is mainly in gaseous form but the gas fraction quickly decreases and represents only 7 % at 5.5 years.

Based on the CAST experimental results, the speciation of C-14 was the following:

- Liquid phase:
    - Inorganic carbon: carbonate
    - Organic carbon: glycolate[1], acetate[1,2,3], formate[1,2,3], oxalate[1], propionate[2],
- Gas phase:
    - Mainly methane[3], Ethene[3] and CO_2[3] were also detected

[1] *CEA: NaOH solution (M5™ and Zr-4 – 14 days and 6 months)*

[2] *Subatech: NaOH solution (M5™, 6 months)*

[3] *SCK•CEN: $Ca(OH)_2$ solution (Zr-4, 6 months)*

As acetate and formate were also detected in blank solutions by CEA and SCK•CEN, a potential contamination cannot be excluded.

3 Carbon-14 release from Spent Ion Exchange Resins (Neeft E.A.C., COVRA)

3.1 *Carbon-14 speciation in resins*

Ion exchange resins are used to reduce the volume of waste by concentrating the radionuclides from fluids, for example, the moderator water. The most common form of synthetic ion exchange resins is polystyrene divinylbenzene in powdered form with diameters from 5-150 μm or in beads from 0.5-2 mm. The resins have functional groups that are to be exchanged with a radionuclide in cationic form such as $^{60}CoOH^+$ or in anionic form such as $H^{14}CO_3^-$. Carbon species in aqueous fluids can be present as dissolved gas, uncharged species and as an anion but only as an anion, carbon-14 can be concentrated by ion exchange resins. The common functional groups in anion exchangers bear nitrogen for example as a tertiary amino group. The affinity typically increases with increasing charge on the exchanging anion and increasing atomic number (decreasing hydrated ionic radii). For anions, a typical series for affinity is [IAEA, 2002:p.6]:

$$F- < CH_3COO^- \text{ (acetate)} < Cl^- < Br^- < CrO_4^{2-} < NO_3^- < I^- < C_2O_4^{2-} \text{ (oxalate)} < SO_4^{2-}$$

Carbon-14 as acetate has a weak affinity and as oxalate a strong affinity. Please note that inorganic carbon is not reported in this series but CO_3^{2-} is expected to have a stronger affinity due to the larger negative charge.

During storage, inorganic carbon is easily to be decomposed by weak acids to CO_2 as understood in the Swedish programme. The carbon dioxide in the air lowers the pH-value in the weakly buffered water. The pH-value is sufficiently low to allow carbonate on the resins to be converted to carbon dioxide, which is released to the water and transported away with the air. Air bubbling of water containing spent ion exchange resins can therefore result in a reduction of inorganic carbon-14 [ARONSSON *et al.*, 2016]. Figure 3.1 shows that the measured pH value is frequently below 6.37, the first pK_a value for the carbonate system. Consequently at these storage conditions, inorganic carbon can be decomposed into gaseous carbon dioxide and water.

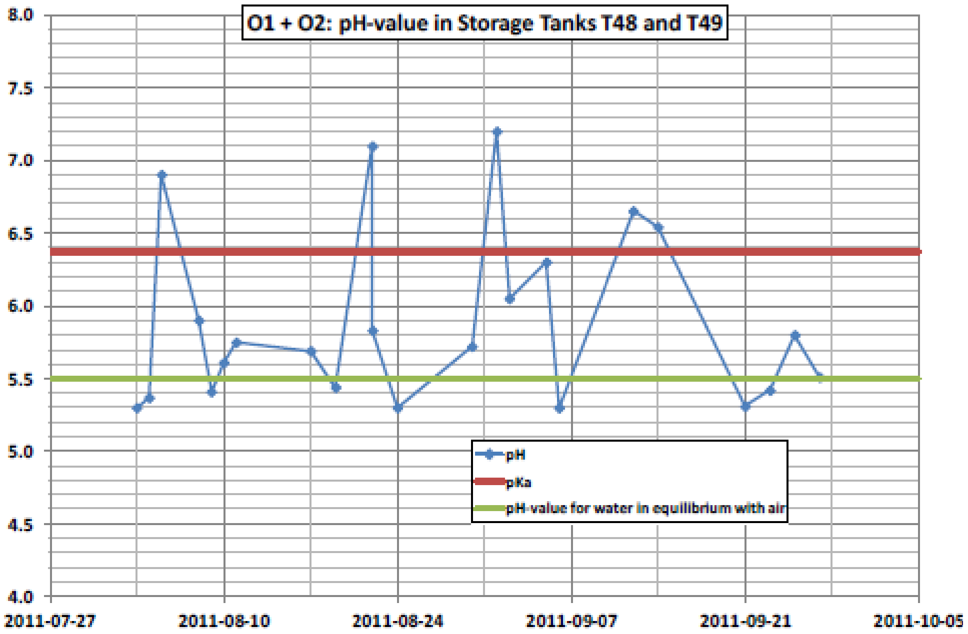

Figure 3.1: pH value (blue) in storage tanks for powder resins at Oskarshamn 1 and 2, August September 2011; pKa value of 6.37 (red) [ARONSSON *et al.*, 2016].

CAST further confirmed that if gaseous release takes place during storage, only inorganic carbon i.e., CO_2 is measured but in alkaline media [BUCUR *et al.*, 2017b (CAST D4.7)]. It is speculative without a carbon-14 speciation what could have caused the CO_2 release but the pH is too high to have a dissolved inorganic carbon origin. An organic carbon origin could be formic acid, this acid has been known to dissociate into CO_2 and H_2 [WIELAND, 2015] but H_2 has not been investigated to be released and it is unknown whether this organic carbon was present in the aqueous fluid. It must be recalled that the alkaline media in these experiments were NaOH [BUCUR *et al.*, 2017b (CAST D4.7)]. In cementitious pore water, the high amount of calcium will fix CO_2 as calcite [REILLER, 2018 (CAST D4.9)].

3.2 Determination of carbon-14 content

Different methodologies have been used in CAST to determine the carbon-14 content [RIZZATO *et al.*, 2015 (CAST D4.1)]. The resins investigated in CAST reports are mainly beads. Beads have a smaller reactive surface area than resins in powder form and consequently the number of actives sites for exchange is for powder larger than for beads. Powders are therefore frequently used from condensate clean-up. Powder resins to clean aqueous fluids from BWRs are Swedish (SKB) and German (FZJ) spent resins. The samples of bead resins to clean aqueous fluids from PWRs have been taken in Sweden, Romania (for CANDU reactors), France and Czech Republic [REILLER, 2018 (CAST D4.9)]. The sample descriptions with which experiments are performed have been described in the state of the art [RIZZATO *et al.*, 2015 (CAST D4.1)] and the first, second and third Annual reports, [REILLER *et al.*, 2014 (CAST D4.2)], [BUCUR *et al.*, 2015 (CAST D4.3)], [COMTE *et al.*, 2017 (CAST D4.4)] and in the compilation of the data in WP4 [RIZZATO *et al.*, 2017 (CAST D4.8)]. The carbon activity concentration expressed per gram of spent ion exchange resins (dry and wet) have become available from the French programme but more work is needed to understand the analytical problems evidenced in wet and dried samples. The order of magnitude in activity concentration was 10^3 Bq per gram of wet and dry resin [RIZZATO *et al.*, 2017 (CAST D4.8)]. Combustion with oxygen yielded a higher measured carbon-14 activity concentration than acidic dissolution [COMTE *et al.*, 2017 (CAST D4.4)] but the order of magnitude of the measured carbon activity concentration is the same. The benefit of the determination of carbon-14 activity concentration using the acidic dissolution methodology is that the carbon-14 activity can be discriminated between inorganic and organic carbon. Another explored technique in CAST was desorption of carbon-14 using LiOH 1M solutions. Also with this methodology, a smaller carbon-14 activity was obtained than with combustion with oxygen [COMTE *et al.*, 2017 (CAST D4.4)].

In the Swedish programme, the inorganic and organic carbon content is measured using acid stripping and wet oxidation as proposed by Magnusson [ARONSSON *et al.*, 2016]. In the acid stripping method, inorganic carbon compounds are decomposed by weak acids to carbon dioxide. Further on, the adsorbed organic carbon is oxidised to CO_2 using potassium persulphate [RIZZATO *et al.*, 2015 (CAST D4.1)]. Using this method, drying in air was measured to reduce the carbon-14 content by three orders in magnitude in spent ion exchange resins [ARONSSON *et al.*, 2016]. In all methodologies used, the inorganic carbon-14 content was measured to be reduced after drying but not the organic fraction [ARONSSON *et al.*, 2016; COMTE *et al.*, 2017 (CAST D4.4)]. In the CAST reports, the carbon-14 content in mainly wet unconditioned samples has been measured. More than 90% was measured to be inorganic carbon for spent resins used to clean aqueous fluids from a BWR, and ca. 70-80% inorganic carbon for PWRs [REILLER, 2018 (CAST D4.9)].

3.3 *Arguments for determination source term*

Processed spent ion exchange resins are already disposed in European countries in near-surface facilities in Sweden, Finland, Hungary, Slovenia, Spain and France [BUCKAU *et al.*, 2016 (CAST D7.11)]. Safety assessments for disposal have been made that resulted in a licence application for disposal of processed spent ion exchange resins. The potential hazardous carbon-14 release originated from the assumption about organic carbon-14: no retardation in cementitious materials. During CAST, the retention of low molecular weight organics in a cementitious environment was evaluated by PSI [CAPOUET *et al.*, 2017 (CAST D6.2)]. Organic compounds as a group including alcohols, aldehydes and carboxylic acids were considered. The retention mechanism of organic compounds discussed in CAST is sorption on cementitious minerals. Another retention mechanism is - like inorganic carbon - precipitation with the dissolved calcium in cementitious pore water. For spent ion exchange resins, a specific group of organic compounds is present i.e., only the dissociated anions from carboxylic acids are exchanged with a functional group in ion exchange resins e.g., acetate from acetic acid and oxalate from oxalic acid. Alcohols and aldehydes dissociate less easily than carboxylic acids and therefore for example alkoxide ions from alcohols are not expected to be concentrated by ion exchange resins. Earlier work in the previous century investigated the precipitation of anions from carboxylix acids such as oxalate in cementitious environments due to the calcium content in cementitious pore water [VAN LOON and HUMMEL, 1995].

Unconditioned wet resins have been investigated in CAST reports and conditioned resins may not reflect the same behaviour [REILLER, 2018 (CAST D4.9)]. Disposed are conditioned resins. From available literature, a few arguments can be made that limit the potential carbon-14 release from resins conditioned with cementitious materials.

Resins are organic matter and are therefore considered as a potential food source for microbes in the EU research project MIND but the usable energy for microorganisms would barely be sufficient to breakdown ion exchange resins [ABRAHAMSEN *et al.*, 2015]. The microbial degradation in intact cementitious materials is also expected to be limited due to space restriction. Microbial activity can therefore be excluded as a factor for potential carbon-14 release.

The chemical resistance of resins is generally larger than inorganic ion exchangers and resins are therefore preferred [IAEA, 2004]. Chemical degradation of organic materials can be initiated by a nucleophilic attack of OH- ions on a carbon atom with a partial positive charge. Such carbon atoms are generally not present in polystyrene, the basic material for ion exchange resins [VAN LOON and HUMMEL, 1995; ABRAHAMSEN, 2015]. A degradation rate of resins representative for the disposal conditions is therefore not yet available. Chemical degradation can therefore be excluded as a factor for potential carbon-14 release.

The potential formation of organic gaseous products e.g., CH_4 and C_2H_6 during disposal is absent and any CO_2 from dissolved inorganic carbon is expected to be released during the waste processing with cementitious materials since the pH values are by far larger than 6.37 i.e., first pK_a value for the carbonate system. There is CO_2 measured in alkaline media in CAST but these media did not contain calcium and may therefore not be representative for waste conditioning in which the calcium dissolved in cementitious pore water will fix CO_2 as calcite.

There is a maximum amount in processing resins with cementitious materials to prevent crack formation of the waste matrix due to the swelling pressure of the resins. A maximum in 20 vol% is recommended [MATSUDA *et al.*, 1992]. In terms of weight due to this processing, the carbon-14 activity in processed waste by resins can be an order of magnitude smaller than the one measured in resins. As input in the calculations performed in CAST by Fortum, 10^3 per gram waste package is conservatively assumed [KENDALL *et al.*, 2015 (CAST D6.1)] which is the same as measured for resins to clean the PWR coolant [CAPOUET *et al.*, 2017 (CAST D6.2)].

The carbon-14 source term of spent ion exchange resins processed with cementitious materials is expected to be very small due to:

- the small carbon-14 activity concentration of about 103 per gram resin which can be reduced in an order in magnitude by waste processing with cementitious materials;
- potential lack of gaseous products such as hydrogen during chemical degradation by which enhanced gas transport can occur;
- potential carbon-14 release is expected to be only be in ionic form since exchanged carbon-14 is present as an anion in anion exchangers i.e., gaseous carbon-14 and neutral dissolved carbon-14 species such as alcohols and aldehydes cannot be concentrated by ion exchange resins;
- high chemical resistance of resins by which its chemical degradation rate has not been measured yet.

4 Carbon-14 release from Irradiated graphite (Norris S., RWM)

This synthesis is based on the Work Package 5 Synthesis Report [TOULHOAT *et al.*, 2018 (CAST D5.19)] and relates to and outlines the behaviour of irradiated graphite in the context of deep geological disposal in a cementitious repository. It must be remembered that some national programmes participating in CAST Work Package 5 do not envisage this approach for the long-term management of irradiated graphite; for example, some consider long term storage in a surface facility or disposal to a near surface / shallow geological facility disposal. A regulatory 'cap' on the total amount of carbon-14 permitted may also be in place. As national programme requirements drive research activities related to irradiated graphite (and other inventory components), these activities themselves may involve considerations of varying end points. Furthermore, the relative importance in the safety case of irradiated graphite-derived carbon-14 (aqueous) versus carbon-14 (gaseous) also can vary by disposal concept; this can affect the prioritisation of research activities.

- 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 reducing over time (i.e., the release cannot be defined by a single rate constant);
- Carbon-14 can be released to both the gas and aqueous phases. Carbon-14 released to the gas phase may exist as a number of different species with potentially different consequences, including organic species (e.g., CH_4), CO_2 and CO;
- Release rates and speciation of the released carbon-14 may change depending on the conditions (e.g., pH, presence of oxygen).

In order to parameterise a model for the behaviour of irradiated graphite in the context of deep geological disposal in a cementitious repository, the following information needs are relevant:

- The initial total activity of carbon-14 in the graphite;
- The fractions of the carbon-14 activity in the graphite that are available for rapid and slower releases (any remaining fraction will not be releasable);
- Rate constants for the rapid release of carbon-14 under each set of conditions;
- Rate constants for the slower release of carbon-14 under each set of conditions;
- The fractions of carbon-14 released as CH_4 and CO under each set of conditions (the fraction not released as CH_4 or CO is assumed to be released as CO_2).

Various sets of conditions can be considered for which input values can be specified. Examples of these are:

- Aerobic, neutral pH: expected to be applicable to waste packaged without grouting;
- Aerobic, high pH: expected to be applicable to grouted waste during GDF operations and early post-closure;
- Anaerobic, high pH: expected to be applicable in the post-closure period, usually after resaturation.

There is a certain degree of empiricism to the above. Although some information regarding the potential mechanisms of release of carbon-14 from graphite has been obtained, the mechanisms are not currently fully understood. Therefore, it is appropriate for a model to represent the important features of the release behaviour observed across various types of experiments. The limitation of this approach is that there will be uncertainty in the release calculated by the model on timescales that are substantially longer than those for which experimental data are available.

Parameterisation needs to be cautious, taking into account the long timescales over which leaching may occur and the variability of the graphite used in different reactors. When longer-term measurements are available it may be possible to reduce the release rates and release fractions.

Work undertaken as part of RWM's programme and the programme of the Lithuanian Energy Institute (Grigaliuniene *et al.* in [HENOCQ *et al.* 2018 (CAST D6.3)]) has led to the following parameterisation being derived. Table 4.1 shows the release model parameters, and Table 4.2 presents speciation parameters (the fraction released as CO_2 is assumed to be the sum of the $^{14}CO_2$ measured in the gas phase (this is only significant for neutral pH conditions) and the total carbon-14 in solution. For high pH conditions, the proportion released as gaseous carbon dioxide is small in comparison to the fractions released as carbon monoxide and methane).

Table 4.1: Parameter values for carbon-14 release

Parameter	Lower bound	Best estimate	Upper bound
Rate constant for the rapid release of carbon-14 from graphite (k_{ca})	10 yr^{-1}	30 yr^{-1}	100 yr^{-1}
Rate constant for the slower release of carbon-14 from graphite (k_{cc})	1 10^{-3} yr^{-1}	1 10^{-2} yr^{-1}	1 10^{-1} yr^{-1}
Fraction of the carbon-14 activity in the graphite that is available for rapid release	0	2 10^{-4}	2 10^{-3}
Fraction of the carbon-14 activity in the graphite that is available for slower release	1 10^{-2}	5 10^{-2}	3 10^{-1}

Table 4.2: Parameter values for speciation of released carbon-14

Conditions	Fraction released as CO_2	Fraction released as CO	Fraction released as CH_4
Aerobic, neutral pH	0.99	0.0050	0.0050
Aerobic, high pH	0.99	0.0050	0.0050
Anaerobic, high pH	0.99	0.0033	0.0066

It must be recalled that these values are not necessarily transferable verbatim for consideration in relation to other waste management organisations' irradiated graphite and its behaviour in the context of deep geological disposal in a cementitious repository.

Part 2 – Upscaling to disposal systems

5 Upscaling to clay disposal systems (Capouet M., ONDRAF/NIRAS)

5.1 *Sensitivity of carbon-14 release in clay disposal systems*

The low permeability of the host formation favours a diffusive migration of the radionuclides in clay disposal system. Because of the relatively short half-life of C-14, its radiological flux released from a waste disposal in clay to the biosphere is particularly sensitive to its transport rate in the host formation.

If the transport is controlled by diffusion (diffusive coefficient D), the flux of N radioelements decaying at rate λ at a distance L from an instantaneous point source is represented by the following solution in one-dimensional system:

$$J\,(t) = \frac{N}{2\sqrt{\pi D t}}\ \frac{L}{t}\ e^{-\frac{L^2}{4\,D\,t}}\ e^{-\lambda t}$$

Figure 5.1 represents the fluxes of two stable tracers (tagged by the exponent of their exponential function) at a distance L from the source and released in same amount. The first is assigned a (unrealistic) high diffusion coefficient (D_1) and the latter, a diffusion coefficient fifty times lower ($D_2 \sim 10^{-10}$ m^2/s) representative of a conservative value for a tracer in a clay formation. The radioactive decay of an arbitrary amount of C-14 ($N_{C\text{-}14}$) is also shown. If the transport time is short (e.g., ~1 000 years), the peak C-14 release rate ($J_{C\text{-}14}(D_1,\ t)$) is comparable to that of a stable tracer. However, if the transport time is long (e.g., several tens of thousands of years), the peak release rate ($J_{C\text{-}14}(D2,\ t)$) is considerably reduced compared to that of a conservative tracer. Clay disposal systems provide thus an excellent performance regarding C-14, provided confinement times in the disposal system are of the order of a few tens of thousands of years. The full containment during at least the thermal phase and the potentially slow release of the waste matrix makes C-14 impact relatively limited in the case of high-level radioactive waste.

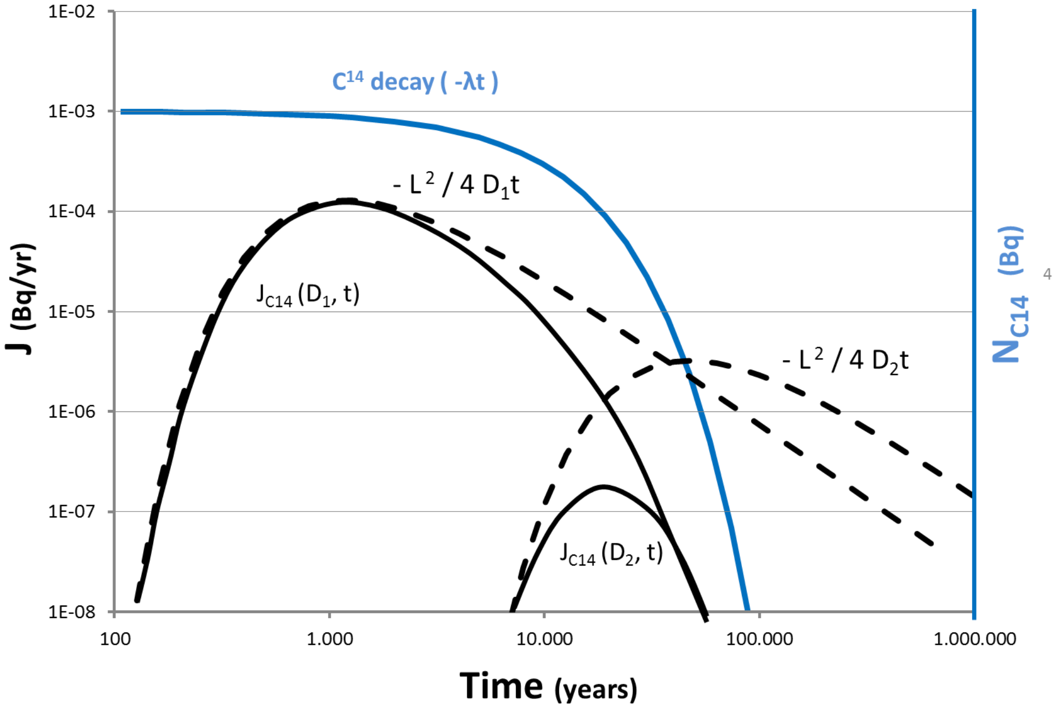

Figure 5.1: Fluxes J at a distance L from a source calculated for a stable element (dashed curves) and C-14 (plain curves), released in same amount and with two different diffusion coefficients (D1 and D2). The radioactive decay of an arbitrary amount of C-14 is also represented (blue plain curve).

The speciation of C-14 has a substantial influence on its transport in clay systems. Kinetic exchange experiments and literature studies carried out by Andra and reported in CAST by HENOCQ *et al.* in [HENOCQ *et al.* 2018 (CAST D6.3)] investigated the inner workings of the C-14 retention mechanism. Inorganic C-14 sorbs on clay rocks and on cement-based materials. The retention of C-14 onto calcite is governed by isotopic exchange between C-14 and C-12 from calcite. Many safety assessment studies consider distribution coefficients for inorganic C-14 on clay in the range between 10^{-4} and 10^{-3} m^3/kg [KENDALL *et al.*, 2015 (CAST D6.1)] leading to typical transport time in the host formation longer than a few tens of thousands of years and a limited radiological impact of C-14 as shown by the sensitivity studies carried out by Mibus in [HENOCQ *et al.* 2018 (CAST D6.3)].

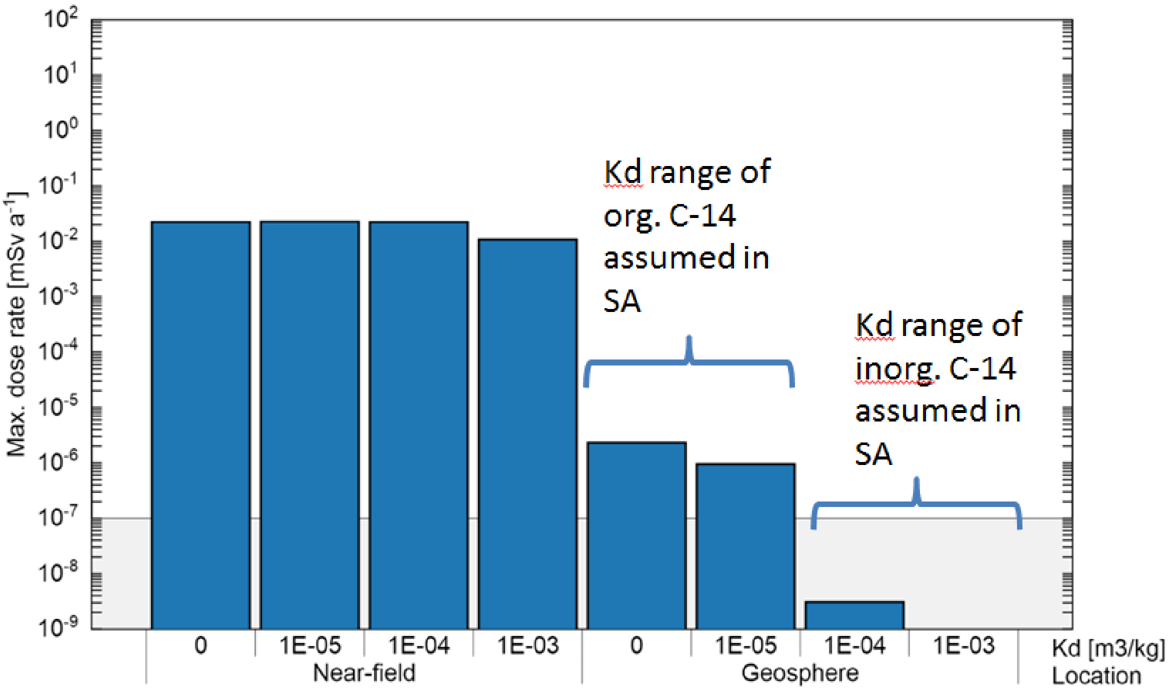

Figure 5.2: Maximum dose rate from the near-field and the geosphere for different sorption values as calculated by Mibus in [HENOCQ *et al.* 2018 (CAST D6.3)]

The performance of the waste form and the engineered barriers with respect to C-14 confinement is usually overshadowed by the efficiency of the clay formation as shown in Figure 5.2. This was also emphasized by Hart *et al.* in [HENOCQ *et al.* 2018 (CAST D6.3)] using probabilistic sensitivity analysis. The sensitivity studies performed in CAST for clay disposal systems have shown that the maximum of C-14 activity flux is almost insensitive to instant release fractions (IRF) up to 20%, except for very low corrosion rates in the case of Zircaloy. However, processes in the near field might reveal to be efficient in binding the C-14 source term of the near field through 1/ Strong C-14 uptake on cement-based materials that compensates the limited EBS thickness and, 2/ The calcite solubility limits in the close environment of the waste. The precipitation of calcite can be particularly efficient to limit the inorganic C-14 releases in scenario of accelerated (instantaneous) waste dissolution [HENOCQ *et al.* 2018 (CAST D6.3)]. These sensitivity analyses show that clay disposal provides a robust defence in depth system to hamper inorganic C-14 release in the biosphere to very low levels.

On the contrary, sensitivity studies show that, in the present state of knowledge, the possible uptake capacity of the C-14 bearing organic components measured in CAST is too low to have a discernible effect on C-14 transport (see studies of Wieland, E. and Chen *et al.* reported in [CAPOUET *et al.*, 2017 (CAST D6.2)]. For C-14 organics, the source term (inventory and waste corrosion/degradation rate) and the diffusive transport are the only two key safety relevant processes.

The organic C-14 might become even more relevant in scenarios where the diffusive capacity of the geological barrier is cut short. That is typically the case in advective scenarios that take place in conditions where a pressure gradient and a permeable path are present and a carrier fluid (e.g., water or gas) is available. The accelerated transfer to the biosphere limits the spreading effect of the diffusive migration and the benefit of the radioactive decay. Furthermore, the discrete transport path results in a more localised release in the biosphere (e.g., through the shaft). The C-14 organic gas scenario in clay systems was investigated by Mibus, Henocq *et al.* and Gray and Carter in [HENOCQ *et al.* 2018 (CAST D6.3)]. In a repository, most gas is expected to come from anoxic metal corrosion and to a much lesser extent by radiolysis and microbial activity. The production of hydrogen can vary several orders of magnitude from a waste type to the other and can be particularly important for ILW metallic waste. The key uncertainties are the metal corrosion rate and the specific surface (e.g., compacted waste from reprocessing). If the capacity for diffusive removal of dissolved hydrogen is exceeded in the near field environment, a discrete gas phase is formed with possible adverse effects: The excessive pressures can induce damage to the multi-barrier system and the creation of a discrete path. The conditions of a scenario of enhanced radionuclide transport, among which volatile C-14, carried by hydrogen are then met. Different strategies have been developed to tackle both the hydrogen pressurisation and the advective transport of C-14. EBS materials and disposal design can be optimised to manage the gas transport in a non-disruptive way and foster diffusive dissipation of hydrogen (e.g., increase porosity and exchange surface with the host formation). Also, increasing the distance between C-14 emitting waste and the shaft to maximise the confinement time and diffusion of volatile C-14 in the clay rock can be a design option. Last but not least, reducing uncertainties pertaining to corrosion rates, amount of metals and specific surface would benefit to the source term of both the hydrogen carrier and C-14.

Capouet in [HENOCQ *et al.* 2018 (CAST D6.3)] considered the effect of hydride embrittlement in a scenario with an instantaneous release of 100% of the C-14 inventory in CSD-C.

The efficiency of the diffusive transport combined to design choices if necessary results in an effective dose for the alternative scenarios discussed above, well below the dose constraint.

5.2 *Implications of the CAST project on clay disposal systems*

The experimental results of CAST have improved the knowledge regarding different factors influencing the C-14 source term. First, at level of the speciation: The presence of a non-negligible fraction of organic C-14 compounds in Zircaloy, steel and SIERs has been confirmed. Due to the uncertainties over the speciation of these compounds and their possible retention mechanism, C-14 organics are considered as weakly or not retarded in safety assessment modelling of clay disposal, to the opposite of the inorganic fraction. The C-14 activity flux released from clay disposal system is thus formed about exclusively of organic compounds.

It follows that reducing the calculated C-14 impact implies reducing the uncertainties pertaining to the source term. In this respect, a reviewing work has been carried out on C-14 inventories of Zircaloy to reduce the uncertainty of the nitrogen concentration. More particularly, literature review and experimental studies have allowed to reduce the uncertainties on the corrosion rates of the metals investigated in CAST. The CAST project has confirmed the very low corrosion rates of Zircaloy and steel in alkaline, anoxic conditions. These low rates imply that a large fraction of C-14 decays in the waste itself before being actually released if the corrosion rate is of the order of nm/year and the IRF is low as well. Experimental studies seem to confirm the negligible IRF for steel. Regarding Zircaloy, there are indications of the capacity of the oxide layer to retain C-14 suggesting that the IRF traditionally assumed between 10 and 20% is over-conservative.

The different scenarios calculated in clay systems (expected and less expected or more conservative) on the basis of the CAST results return radiological impacts lower than the radiological requirements.

6 Upscaling to crystalline disposal systems (Nummi O., FORTUM)

Crystalline rocks are selected as host rocks for radioactive waste disposal due to their stability, high strength and low permeability. In crystalline rocks, groundwater flow takes place through the open fractures. Locating the repository caverns in crystalline rocks away from the major fracture zones at a sufficient depth limits the groundwater flow through and in the vicinity of the repository caverns. This provides more favourable near-field conditions for the engineered barrier system, limits the radionuclide transport and isolates the waste from the biosphere.

The safety of the disposal can be based on (i) the characteristics of the waste (activity and release rate), (ii) the performance of the engineered barrier system, and (iii) a favourable repository location in bedrock. The radionuclide migration through the engineered barriers and bedrock can be retarded by radionuclide sorption - however the impact is very limited or even non-existent for non-sorbing or weakly sorbing radionuclides such as C-14 (in organic form), Cl-36 and I-129. As an example, Figure 6.1 demonstrates the low impact of geosphere retention on the radionuclide release rates, when all C-14 is assumed to be released and migrate in a non-sorbing, organic form.

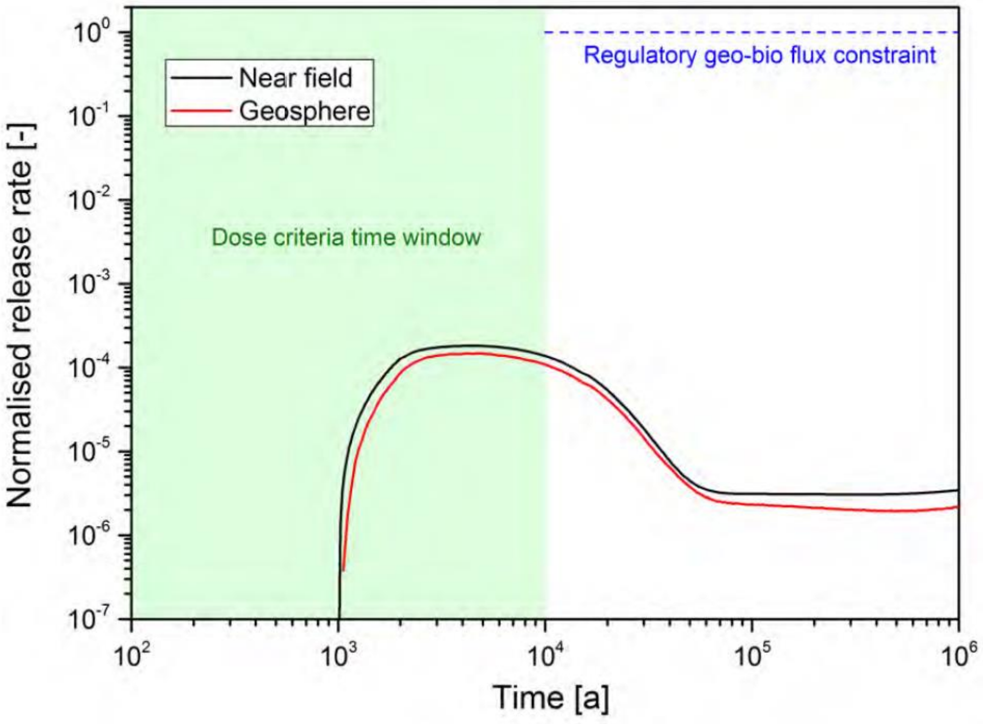

Figure 6.1: Near field and geosphere release rates in the reference case of Posiva's TURVA-2012 safety case for disposal of spent nuclear fuel at Olkiluoto [POSIVA, 2012]. The release rates have been normalised with respect to nuclide specific regulatory constraints for releases into biosphere. During the first tens of thousands of years the total normalised release rate is dominated by C-14.

Based on experimental results from the CAST project, the majority of C-14 released from the activated steels and Zircaloy exists in organic, low sorbing form. The speciation of C-14 released from the ion-exchange resins is strongly dependent on the power plant type, the ion-exchange resins storage and conditioning prior to disposal [REILLER, 2018 (CAST D4.9)]. The CAST results mostly confirm the earlier, conservative assumptions regarding C-14 speciation applied in the safety assessments [KENDALL *et al.* 2015, (CAST D6.1)], but considerably reduce the uncertainty in the C-14 speciation released from the waste. The remaining uncertainty in the speciation of C-14 has only a relatively small impact on the safety assessment results in comparison to other uncertainties, for instance C-14 release rates and the performance of engineered barrier system.

In crystalline rocks, the open fractures also provide pathways for the gas transport, including radionuclides in gaseous form. As a consequence, the C-14 released and migrated in organic gaseous form are expected to migrate at a rate comparable to organic C-14 dissolved in groundwater [HENOCQ *et al.*, 2018 (CAST D6.3)]. This may, however, vary between different repositories.

In addition, CAST project provided further insight on the C-14 release rates from various waste materials. The release rates are determined by C-14 activity in the waste, congruent release rate and instant release fraction. Especially, the low corrosion rate of activated steels and Zircaloy under alkaline conditions can lead to a considerable radioactive decay of C-14 prior to its release from the waste. In addition, experiments outside the CAST project indicate a weak sorption of organic C-14 into cementitious materials that may retard the C-14 release from the near-field.

The overall impacts of these findings depend on their incorporation into safety assessments, on the disposal concept and to the overall impact of C-14 assessment and the handling of C-14 in the biosphere assessment. An example of impacts of increased understanding gained during the CAST project in Lithuanian Energy Institute's (LEI's) modelling approach is discussed by Grigaliuniene *et al.* in [HENOCQ *et al.*, 2018 (CAST D6.3)]. The comparison between near-field release rates calculated before and during CAST project are shown in Figure 6.2. However, the sensitivity analyses carried out by LEI, SURAO and Fortum [HENOCQ *et al.*, 2018 (CAST D6.3)] indicate a strong impact of near-field groundwater flow rates and sorption (including the uncertainty in the speciation) on the release rates.

The uncertainties in the C-14 source term that remain after the CAST project are the long-term corrosion rates of steel and Zircaloy, release rates from graphite as well as the speciation of C-14 released from all the waste types. Additionally, the change in speciation of C-14 bearing species during the migration (e.g., due to microbiological activity) remains unknown, with a potential impact on C-14 migration released both in organic or inorganic forms.

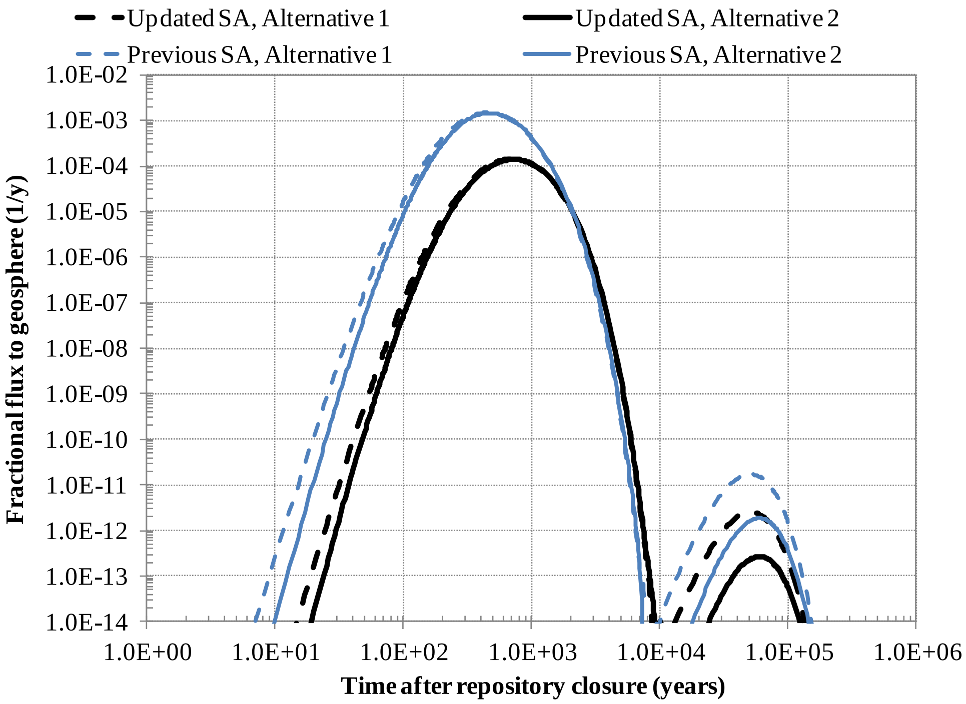

Figure 6.2: Fractional near-field release rates before CAST and updated based on CAST project in the safety assessment for LEI indicating increased understanding of the C-14 release from graphite and near-field migration [HENOCQ *et al.*, 2018 (CAST D6.3)].

7 Upscaling to salt disposal systems (Rübel A., GRS)

The long-time separation of the radioactive waste from the biosphere in the case of a waste disposal in a salt host formation relies on the salt material. This is on the one hand the undisturbed part of the salt host rock formation and on the other hand the crushed salt, which is used to backfill the mine openings in the emplacement areas and galleries. The crushed salt backfill is compacted over time and achieves a sufficiently high hydraulic resistance to avoid entries of brines into the emplacement areas of the repository. Plugs and seals must provide their sealing function during the early post closure phase, until the compaction of the backfill is adequate and the permeability of the backfill is sufficiently low. At a certain stage, backfill and host rock both have a permeability in the same order of magnitude.

For salt repository concepts, the expected evolution is marked by very dry conditions. Sources of water are the brine inflow, which is very slow, but also water emplaced together with the waste or the backfill. Corrosion processes is expected to be limited by the availability of water. Due to the unsaturated conditions prevailing over very long times in the expected evolution of dedicated salt repositories, gas transport is dominated by advection in the gas phase. In case of low liquid saturation, gas can flow without needing to displace the liquid phase.

For a potential release of C-14 from the repository in salt, therefore, the amount of release to the gas phase and its subsequent transport in the gas-phase are the primary questions for the potential contribution of C-14 to the overall radiation exposition in the biosphere.

A flow of non-radioactive gases in the mine is caused from the beginning of the post-closure phase. The origin of this flow is the displacement of air from the repository mine due to salt convergence and the generation of gases in the mine due to waste degradation. The rock convergence, gas and liquid flow are coupled processes: On the one hand convergence will increase the pore pressure and therewith initiate gas flow. On the other hand, the flow of gas will modify the pore pressure, and thus act on the compaction rate. This interplay can lead to a complex flow pattern inside a repository built in rock salt. For heat generating wastes an additional effect plays a role: Since convergence and compaction of crushed salt strongly depends on temperature, there is an initial gas flow from hot areas (converging faster) to cold areas (converging slower).

The salt host rock itself is impermeable for gas at pressures well below the minimum principal stress. Gas flow will therefore follow preferential flow paths given by the engineered barrier system (EBS), the excavation disturbed zones (EDZ), and material interfaces. Gas will cause macroscopic fractures in the host rock if gas pressure reaches the minimum principal stress of the rock. Due to stress heterogeneities at the microscopic scale gas will already infiltrate at slightly lower pressures on grain boundaries without compromising the host rock's integrity.

The boundary conditions of the experiments performed in the CAST project do not match the ones expected in the reference evolution of a repository in salt. This is

1.) because of unsaturated conditions prevailing over the time of interest for the release of C-14, while experiments in CAST have been performed under saturated conditions,
2.) because of the fact that those small amounts of fluids existing in the repository show salt concentrations at saturation while the experiments in CAST have been performed with low mineralized waters and
3.) because of the temperatures in a repository concept for high-level waste in salt are likely to be chosen much higher than the 100°C considered in other types of repository concepts and in the experiments of CAST.

Therefore, the results from the CAST project cannot be directly transferred to the safety case of a repository in salt. For the release of C-14 from Zircaloy claddings of spent fuel, there are indications in CAST that the source-term of C-14 is dominated by the release from the oxide layer and that 1 % of the C-14 inventory is a maximum ratio to account for the very low fraction of accessible C-14 that is released. Since the release mechanism is relatively unknown, the validity of the data for the conditions in salt is questionable. Intermediate results indicate that the fraction of organic compounds exceed fraction of inorganic and that the organic speciation might be organic gas. This means that the released C-14 is in a phase that potentially can be transported in the unsaturated backfill of the repository. The volatile fraction of C-14 in the atmosphere of the fuel rod of the assembly is stated to be below 0.2 % according to findings in the First Nuclides project [KIENZLER *et al.*, 2014] which contradicts previous findings of high fractions of C-14 by Smith and Baldwin (1993). This is an issue that has still to be discussed in the future.

For steels a congruent release of C-14 with corrosion of the material is assumed. The instant release fraction is assumed to be very low. If the availability of water is limited in the repository in salt host rock, this also could substantially limit the release of C-14. Very low corrosion rates have been determined in CAST that are however not applicable to the situation of a repository in salt due to the differences in temperature and mineralisation of the solution. The statement of congruent release however still could be used as basic assumption with specific corrosion rates for salt derived for non-radioactive material from other projects.

For ion exchange resins, the situation is more difficult since those are very heterogeneous in type (resins, immobilisation process, processing conditions) and inventory because of their different origin. The C-14 release from these resins might more be depending on the resin type than the disposal option. Therefore, the bandwidth of the results given in CAST is rather high and the results have to be further evaluated to be transferred to the different national contexts considering a disposal option in salt.

In the CAST project, two groups performed simulations to assess the contribution of C-14 to the dose, the influence of source term parameters on the dose and the implications of the CAST results. These are ENEA from Italy for a repository for low- and intermediate level and GRS from Germany for a repository for high-level wastes.

7.1 Simulations by GRS

TOUGH2 was used to model the gas and radionuclide transport in a repository for high-level waste, i.e., spent fuel, compacted metal wastes and vitrified wastes. A flow of non-radioactive gases in the mine is caused from the beginning of the post-closure phase by the displacement of air from the mine. This is due to the convergence of the salt host rock and the decreasing porosity in the salt grit. Additionally, a flow of hydrogen gas results from the iron corrosion by the small amount of water initially emplaced with the containers and the salt grit backfill. External waters might reach the emplacement fields closest to the shaft and can potentially lead to a more significant corrosion and gas production. However, this would occur at later times which are not relevant for the C-14 release. The C-14 instantaneously mobilised from the instant release fraction (IRF) of the Zircaloy is released from the four initially defect spent fuel containers directly at the beginning of the post-closure phase and is transported further on along with the non-radioactive gases through the unsaturated drifts to be released through the drift seal. The IRF of the spent fuel matrix or material in the CSD-C containers is assumed to be mobilised only in contact with water which is only limited at the beginning. CSD-V waste is assumed to have no IRF.

Parameter variations were performed to vary the main influencing factors of the source term, i.e., IRF, the release rate and the release start time. As a summarizing conclusion it can be stated that the consequences of the C-14 release from the waste in the early phase of the repository are to a large part controlled by the quantity of the C 14 released. The temporal behaviour of the C-14 release only shows a minor impact if not delayed significantly. The conservatism in the assumption used before regarding the amount of C-14 released during the early phase of the repository can be significantly reduced thanks to the results obtained in the First Nuclides and the CAST projects. However, these assumptions have to be further justified.

The highest priority to further reduce the uncertainty on the release behaviour of C-14 is mainly related to the question whether water is necessary to transfer C-14 into volatile form or if this does occur also without the presence of humidity.

7.2 Simulations by ENEA

A preliminary evaluation of the radiological impact of gaseous C-14 under geological disposal conditions in salt rock has been performed. Although in Italy there is still no defined project about GDF, current work may support future Safety Assessment studies for a geological repository. In the framework of Italian radioactive waste, the percentage of C-14 bearing waste to be disposed in a possible geological repository is low. Data about radioactive HLW-LL and ILW inventory has been collected to simulate production and migration of gaseous C-14 in a hypothetical repository; irradiated graphite is the most important radiological source. Two simulations with TOUGH 2.0 code have been performed: the first one has preliminary evaluated the radiological impact of gaseous C-14 referred to the whole inventory; the second simulation has evaluated the impact of the graphite alone. In order to work round the limitations due to the lack of data, some conservative assumptions have been used. A preliminary sensitivity analysis has been carried out, highlighting the importance of the geometry and the distribution coefficients in materials used to seal the disposal areas within salt formation. Results of simulations have showed the possibility to correlate the Kd values, the volume and the location of sealing materials to the amount of C-14 emitted toward the surface. More realistic results would be obtained reducing the grid discretization and using more accurate details about repository and host rock.

7.3 Conclusions

The situation in a repository for radioactive waste in a salt formation is characterised by dry and unsaturated conditions. Therefore, transport in the gas phase is dominating radionuclide transport for a long time. Due to the convergence of the backfill, an effective mechanism exists that transports gases out of the repository by advection. In case of low liquid saturation, gas can flow without needing to displace the liquid phase. For a potential release of C-14 from the repository in salt, therefore, the amount of release to the gas phase and its subsequent transport in the gas-phase are the primary questions for the potential contribution of C-14 to the overall radiation exposition in the biosphere.

Early release of C-14 to the gas phase can be relevant either from C-14 that is already present in the gas phase at the time of emplacement which is released from non-gastight containers or that is generated by contact of the waste with the low amount of water initially present. The latter is especially relevant if waste forms are emplaced that contain fractions of water. Water is expected to be a limiting factor for C-14 generated by corrosion processes. One of the main remaining questions is whether water is necessary to transfer C-14 into volatile form or whether there are processes that this also occurs without the presence of humidity.

For altered evolution scenarios or at later times, the waste might get in contact with larger amounts of water. There are increasing indications that the gaseous release of accessible C-14 from both the Zircaloy (oxide layer), the spent fuel rod and the steel are relatively low (1%, all together). However, the experimental conditions of CAST are not directly representative of these prevailing in a salt disposal. This could especially affect the C-14 generation rates. The corrosion rates of metals (and hence the C-14 generation rates in case of congruent release) are expected to be higher in high saline brines as under the conditions applied in CAST.

The safety assessment simulations have shown C-14 in the gas phase to be a relevant radionuclide. This shows the need for additional research and development to reduce potential uncertainties and conservatism. The calculated C-14 fluxes highly depend on the assumptions regarding time and form of the C-14 release. Therefore, the highest priority is to reduce the uncertainty on the release behaviour of C-14. This is mainly related to three questions:

1. Which is percentage of C-14 which can be released into volatile form?
2. Which is the temporal behaviour of the release?
3. Is water necessary to transfer C-14 into volatile form or does this occur also without the presence of humidity?

An additional area of investigation is the optimisation of the repository design to delay a potential release of volatile C-14. A possible option would be construction of gas storage areas inside the repository.

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