CArbon-14 Source Term

CAST

Final Synthesis Report of Spent Ion-Exchange Resins ^{14}C Source Term and Leaching (D4.9)

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CAST – Project Overview

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

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

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

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

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Final Synthesis Report of Spent Ion-Exchange Resins ^{14}C Source Term and Leaching (D4.9)

Executive Summary

This report proposes a short synthesis of the main results of the CAST WP4 activities on estimation of source term, speciation, and release of ^{14}C from spent ion-exchange resins (SIERs). It comes after the results exposed in deliverables D4.5 to D4.7, and comprehensive compilation from D4.8.

It is confirmed that the major part of the ^{14}C source term in SIERs is in inorganic form: more than 90% in BWR samples, and *ca.* 70-80% in PWR samples; the organic forms are mainly short chained organic acids (formate, acetate); a small amount of gaseous release can be obtained, in inorganic form (CO_2); a strong alkaline solution is necessary to leach ^{14}C from SIERs; no leaching from the cemented SIERs samples was observed.

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1. Introduction

1.1 General context and limits of this document

The Work Package 4 (WP4) of the project CAST dealt with one type of radioactive waste containing ^{14}C: Spent Ion-Exchange Resins (SIERs). All the experimental works done within this Work Package have been prepared after a State of the Art Report (SOAR) [RIZZATO *et al.*, 2014], where the types of SIERs samples and analytical techniques were presented and justified. This final synthesis report will recall the main results that are available in the previous annual reports [REILLER *et al.*, 2014; BUCUR *et al.*, 2015; COMTE *et al.*, 2017], and in the compilation and final technical reports on the different tasks [BUCUR *et al.*, 2017; RIZZO *et al.*, 2017; VEČERNÍK *et al.*, 2018]. A more detailed analysis providing compilation and comparison of results is already available in RIZZATO *et al.* [2017]. For the sake of conciseness, and to avoid repetition of existing text in the previous deliverables (D4.1-D4.8), the reader is invited to refer to the previous documents — and references therein — for more complete information.

SIERs are widely used in nuclear facilities for the purification of reactor cooling circuits or waste streams from activation products (*e.g.* ^{14}C or ^{60}Co) or some fission products (^{60}Co or ^{99}Tc) [RIZZATO *et al.*, 2014]. Particularly in pressurized water reactor (PWR) the major contribution of ^{14}C in the resins comes from the clean-up of the coolant circuits, whereas in boiling water reactor (BWR) it comes mainly from the condensate treatment circuit [RIZZATO *et al.*, 2014]. Generally, purification of the various circuits — *i.e.* primary circuit, secondary circuit or effluent treatment — is ensured by a chain of filters and demineralizers using ion exchange resins (IERs). A combination of cationic, anionic, and/or mixed bed resins are used depending on the physicochemical conditions of the circuits and on their specific needs.

At the end of the service, SIERs are discharged from the nuclear facility. At this stage SIERs are often mixed together, *e.g.* in French PWR. Their ionic charge and activity depend on the following criteria:

- chemical or radiochemical saturation;
- maximum service lifetime;
- unusual pressure drop behaviour;
- the fluid quality.

When the criteria thresholds are reached, SIERs are discharged and stored under water in storage tanks. The storage delay may last some months until the dose rate induced by the radioactive decay of the short-lived activation products is low enough to allow handling; then SIERs are conditioned for further application or storage at the nuclear facility, or disposed of.

As SIERs are often planned to be disposed of in a subsurface repository in a cementitious environment, an uncontrolled release of ^{14}C from spent ion exchange resins (SIERs) is of high concern. Thus, the understanding of SIERs' behaviour in disposal-relevant conditions and the release behaviour of radionuclides is a critical step in the development of a safe disposal concept.

1.2 Type of samples used by the WP4 partners

The different SIERs samples used by the WP4 partners are recalled in Table 1 from D4.5 [RIZZO *et al.*, 2017]. The reasons for these choices are full discussed in the SOAR [RIZZATO *et al.*, 2014].

Table 1. Description of the SIER samples collected by the partner [RIZZO *et al.*, 2017]. More details in RIZZATO *et al.* [2014].

Partners	SIERs type	Notes
EDF-CEA (F)	• SIERS from 5 different EDF nuclear reactors (PWR) • Non-irradiated IERs	Wet and dry beads (mixed anionic and cationic)
ENEA (I)	• IERS from PWR Trino NPP • non irradiated IERs stored for 10 years and of recent production	Wet beads (mixed anionic and cationic)
FZJ (D)	• SIERs from BWR (S)	Wet and dry powder (mixed anionic and cationic)
RATEN-ICN (RO)	• SIERs from Cernavoda NPP storage tanks or non-fuel contact purification system	Wet and dry beads (mixed anionic and cationic)
SKB (S)	• SIERS from Condensate Clean-up (BWR) • SIERS from Reactor Water Clean-up (PWR)	Wet and dry beads (mixed anionic and cationic)
ÙJV (CZ)	• SIERs from PWR and Research Reactor	Wet beads (mixed anionic and cationic)

1.3 Experimental techniques

All the partners analysed ^{14}C using a typical *modus operando* with variation as a function of available apparatus: *i.e.* acid stripping followed by combustion (inorganic) or oxidation (organic), and then liquid scintillation counting. This has limited the limit of detection compared to more sensitive techniques such as accelerated mass spectrometry (AMS). Attempts to use ion or gas chromatography, and electrospray ionisation mass spectrometry were not successful.

2. ^{14}C Content of SIERs and inorganic/organic repartition

The main results can be retrieved from the various annual reports and the dedicated final report [RIZZO *et al.*, 2017].

As it was already noted in the SOAR [RIZZATO *et al.*, 2014], the ^{14}C source term in SIERs is under the form of anions from the carbonate system — *i.e.* HCO_3^-, CO_3^{2-}, considered as inorganic carbon — and short chained carboxylic acids — mainly formate ($HCOO^-$) and acetate (CH_3COO^-), considered as organic carbon. The proportion between inorganic and organic fractions was considered as mainly inorganic in the case of BWR; a more important fraction of organic ^{14}C was considered for PWR. As the origin of the SIERs samples were not easy to retrieve — due to *e.g.* mixing of resins from different location within the facilities — drawing general conclusions on the results from available SIERs samples is not an easy task to tackle.

The different results obtained within WP4 seem to confirm the observed tendencies. In the case of BWR more that 90% of ^{14}C 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 ^{14}C, whilst for “industrial” PWR around 20-30% of organic ^{14}C was obtained. The case of the Czech research reactor would need further experiments and information to understand the obtained inorganic/organic repartitions.

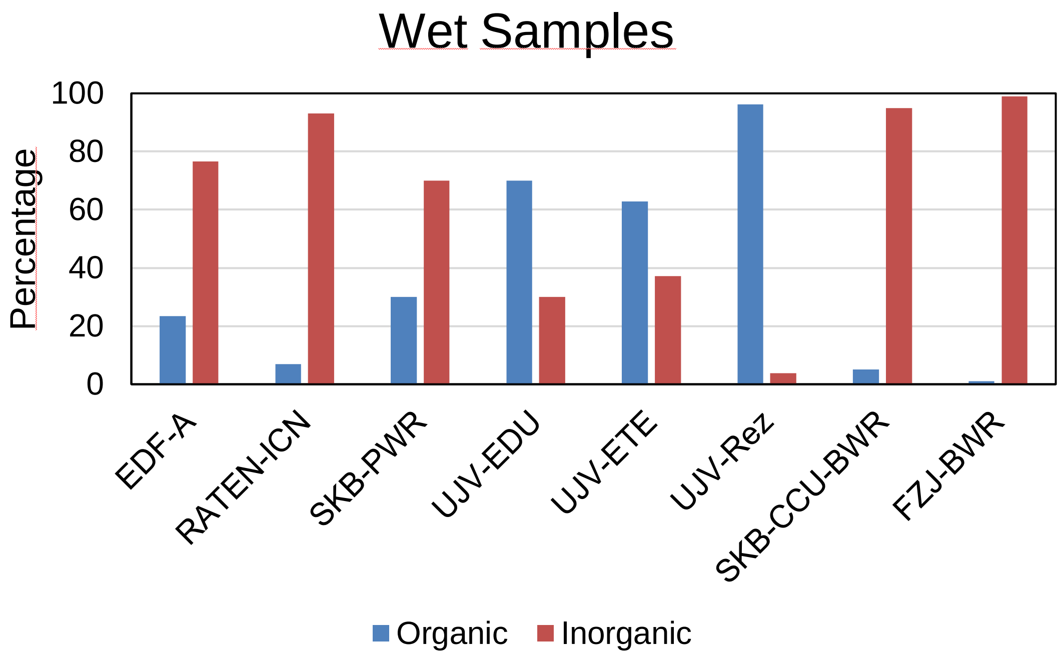

Figure 1. Organic/Inorganic percentage for sample — from Figure 39 in VEČERNÍK *et al.* [2018], built from results in RIZZO *et al.* [2017].

3. ^{14}C Release from SIERs

3.1 Gaseous release

The main results can be retrieved from the various annual reports and the dedicated final report [BUCUR *et al.*, 2017]. Gaseous release was tested under the SIERs samples storage conditions, and in alkaline conditions (NaOH), which were chosen as a simplified medium for cementitious environment.

The gaseous release from the SIERs samples from WP4 has only been possible for BWR (FZJ samples) and PWR-CANDU (RATEN-ICN). It was observed that:

- No detectable gaseous release was detected under storage conditions;
- A small amount (7 to 10 %) of gaseous release was obtained under alkaline conditions in inorganic form.

It must be recalled that in a cementitious environment, a high amount of calcium will fix the gaseous inorganic form (CO_2) as calcite.

3.2 Leaching and desorption

The main results can be retrieved from the various annual reports and the dedicated final report [VEČERNÍK *et al.*, 2018].

Different leaching experiments were done during WP4:

- leaching or SIERs samples under neutral or alkaline pH conditions;
- leaching of cemented samples.

The experiments in neutral to alkaline pH conditions showed that only highly basic media (alkaline hydroxide > 0.1 M) can induce a significant ^{14}C release from SIERs: 90% of ^{14}C seems to be in inorganic form (dissolved carbonate ions).

No ^{14}C release has been observed from the leaching of cemented samples, as awaited from the previous results on leaching in alkaline hydroxide media, and calcium content of cementitious pore water.

4. Conclusions and Outlook

Even if the results from WP4 are inherently limited by the amount of available samples in Table 1 — except the SKB program [ARONSSON *et al.*, 2016] — some general comments can be made:

- It is confirmed that the major part of ^{14}C source term in SIERs is in inorganic form, *i.e.* as part of the anions from the carbonate system: more than 90% for SIERs from BWR, and more than 70% from PWR;
- The organic fraction of the ^{14}C source term is mainly found as short chained organic acids, *i.e.* formate or acetate;
- A gaseous release has only been observed under alkaline conditions, and in the form of inorganic ^{14}C;
- The leaching of ^{14}C from SIERs has only been observed under strongly alkaline conditions;
- The leaching of ^{14}C from cemented SIERs has not been observed.

As noted in RIZZATO *et al.* [2017], it is nevertheless advised that a "*systematic collection and investigation of SIERs from different water-cleaning circuits would favour a better understanding of the source term for 14C and could allow an optimization of the storage conditions in order to prevent uncontrolled release of 14C. This could also support the development of an effective treatment process in order to transfer SIERs into more robust waste-forms for long-term disposal*". It is also recalled that the "*mechanisms evidenced in the present work, however, have been obtained for unconditioned SIERs. National strategies for the management of SIERs are different and conditioned/treated SIERs may not reflect the same behaviour*"

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