Nuclear Engineering and Technology 55 (2023) 2107–2111

Contents lists available at ScienceDirect

Nuclear Engineering and Technology

journal homepage: www.elsevier.com/locate/net

Original Article

Organic and inorganic carbon-14 in discharges of JSC Institute of Nuclear Materials

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ARTICLE INFO

Article history:
Received 11 January 2023
Received in revised form
27 February 2023
Accepted 17 March 2023
Available online 15 May 2023

Keywords:
Carbon-14
Airborne releases
Research nuclear reactor
Catalyst
effective dose

ABSTRACT

The aim of the study is the activity concentration measurements of organic and inorganic ^{14}C in the discharges of JSC "Institute of Nuclear Materials" (INM). In INM the research water-water reactor "IVV-2M" is operating. Collecting of ^{14}C species was performed using a ^{14}C sampler with a chromium oxide and platinum catalysts at different temperatures: 400, 550 and 700 °C. The measurements of ^{14}C activity were performed using a liquid scintillation counter. The share of organic ^{14}C in emissions ranged from 0.30 to 0.84 and depends on the temperature of the catalyst, core structure and reactor operating mode.

1. Introduction

Carbon-14 is a low-energy beta-emitting radionuclide that is produced both naturally and artificially. The natural way is based on the interaction of thermal neutrons and nitrogen-14 atoms in the upper layers of the troposphere and stratosphere: $^{14}N(n,p)^{14}C$. About $1.4 \cdot 10^6$ GBq ^{14}C annually produces this way, while the total amount of ^{14}C in the atmosphere is estimated at $1.4 \cdot 10^8$ GBq [1].

Nowadays discharges from nuclear fuel cycle facilities are the main anthropogenic source of ^{14}C entering the atmosphere [2]. During the operation of a nuclear reactor, ^{14}C is formed mainly as a result of the interaction of thermal neutrons and ^{14}N, ^{13}C, ^{17}O atoms present in fuel elements, structural materials, moderator and coolant, as well as due to uranium and plutonium ternary fission reactions in nuclear fuel [3].

Emissions of ^{14}C into the atmosphere are mainly in the form of $^{14}CO_2$, except for pressurized water reactors [3]. The chemical forms of ^{14}C in airborne releases from various types of reactors are presented in Table 1.

Due to PWRs operate under reducing chemical conditions in the presence of excess hydrogen, a major part of the ^{14}C present in the reactor coolant will be in the form of organic compounds. Consequently, the gaseous releases comprise mainly ^{14}C-hydrocarbons such as methane [4].

If we analyze the discharges from nuclear power plants with light water reactors (Table 2) [5–7], it becomes obvious that the contribution of the organic fraction of ^{14}C cannot be neglected. It can account for up to 97% of total ^{14}C emissions. Besides, ^{14}C makes a significant contribution to the effective dose of population from European NPPs discharges: from 14 to 94 %. ^{14}C also accounts for 12–39% of all released activity [8].

The differences of $^{14}CO_2$ share in discharges of NPP with the same type of reactor can be caused by features of technological processes and conditions for the formation of emissions, as well as sampling method and it's frequency.

Radiocarbon in the discharges of Russian nuclear enterprises is a relatively new component of control, and there is not enough reliable data on the ^{14}C concentration. The object of this study is the composition of ^{14}C releases from the Institute of Nuclear Materials (INM). In INM the research pool-type water-water reactor IVV-2M is operating. Light water is used as a moderator and coolant. The

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https://doi.org/10.1016/j.net.2023.03.019

Table 1
Chemical forms (relative percentage of each species) of ^{14}C in airborne releases from various types of reactors [3].

	$^{14}CO_2$	^{14}CO	^{14}C hydrocarbons
PHWR (Bruce-7, Canada).	65.5–72.8	0.2–3.7	26.7–34.4
PHWR (Gentilly-2, Canada).	77.9–97.5	0.01–0.09	22.0–25.0
PWR (USA and Europe).	5.0–25.0	–	75.0–95.0 (CH_4 and C_2H_6)
BWR (USA and Europe).	80.0–95.0	–	5.0–20.0

Table 2
The share of$^{14}CO_2$ in European LWR discharges.

Site	Reactor type	Period	Reference	$^{14}CO_2$ share		
				Average	Min	Max
Almaraz	PWR	2010–2020	[5].	0.32	0.12	0.84
Asco	PWR	2008–2020		0.31	0.07	0.59
Biblis B	PWR	1995–2011		0.17	0.07	0.44
Brokdorf	PWR	1995–2019		0.42	0.17	0.67
Emsland	PWR	1995–2019		0.61	0.39	1.00
Grafenrheinfeld	PWR	2003–2015		0.26	0.06	0.48
Grohnde	PWR	1998–2019		0.15	0.06	0.32
Isar 2	PWR	2000–2019		0.48	0.17	0.94
Neckarwestheim 1	PWR	1995–2011		0.06	0.02	0.24
Neckarwestheim 2	PWR	1995–2019		0.56	0.29	0.85
Obrigheim	PWR	1995–2005		0.33	0.12	0.98
Philippsburg 2	PWR	1995–2019		0.25	0.07	0.40
Stade	PWR	1995–2003		0.18	0.14	0.23
Unterweser	PWR	2005–2011		0.05	0.01	0.11
Trillo	PWR	2013–2020		0.19	0.09	0.42
Vandellos 2	PWR	2013–2020		0.50	0.19	0.66
Kozloduy	VVER	2010–2020		0.09	0.06	0.11
Krsko	VVER	1991–1996	[6].	0.43	0.43	0.43
Paks	VVER	2005–2020	[5].	0.05	0.03	0.08
		1988–1991	[7].	0.05	0.05	0.05
Bohunice	VVER	2004–2019	[5].	0.18	0.03	0.96
	V213 V230	1991–1996	[6].	0.05 0.20	0.05 0.20	0.05 0.20
Mochovce	VVER	2004–2019	[5].	0.17	0.05	0.94

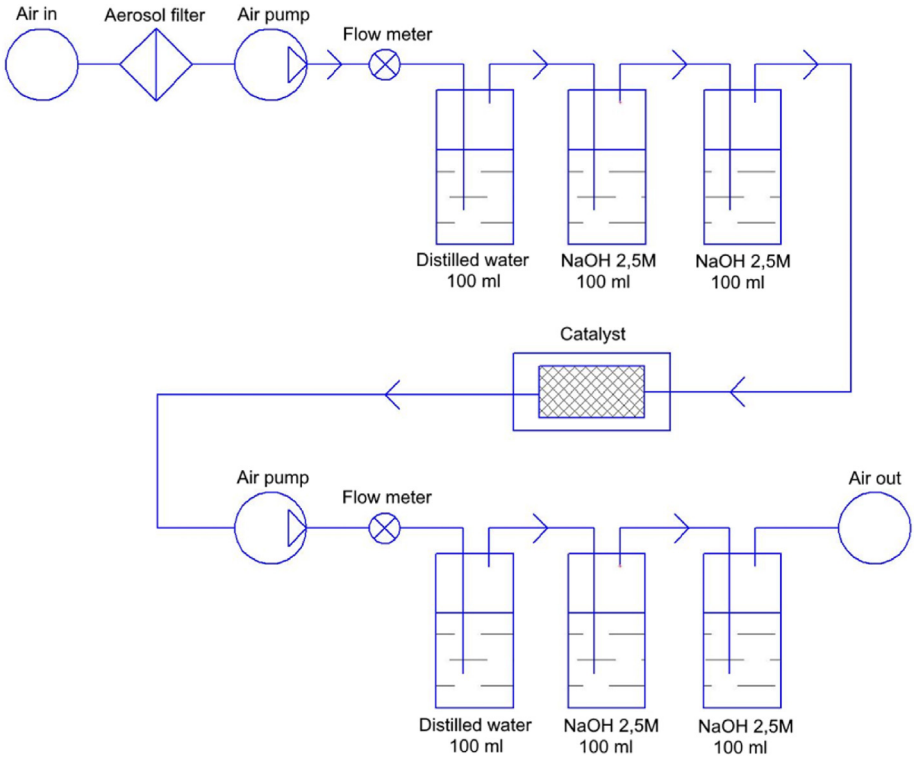

Fig. 1. Scheme of ^{14}C sampler.

nominal thermal power of the reactor is 15 MW. The reactor pool is located in a concrete mass, in a stainless-steel tank [9].

The IVV-2M reactor is operated for radioisotope production (^{14}C, ^{131}Cs, ^{177}Lu, ^{192}Ir) as well as research in the following fields [9]:

- solid-state physics and nuclear physics;
- neutron physics;
- structural materials and biological protection materials;
- effect of ionizing radiation on devices, sensors, semiconductor materials and equipment;

During operation of the IVV-2M reactor, the formation of various radionuclides is inevitable, including ^{14}C, which subsequently enter the atmosphere and the environment with emissions from the high-altitude stack of INM. The sources of carbon-14 formation at INM are such as follow:

- interaction of thermal neutrons with nitrogen-14, present in the coolant and moderator, as well as structural materials: $^{14}N(n,p)^{14}C$;
- interaction of thermal neutrons and oxygen-17 present in the coolant and moderator, as well as structural materials: $^{17}O(n,\alpha)^{14}C$;
- handling of ^{14}C isotope resulting from neutrons interaction with aluminum nitride (AlN) for commercial production;
- spent nuclear fuel handling;
- triple fission of fuel nuclei.

The aim of this article is to determine the activity concentration of organic and inorganic ^{14}C in the discharges of INM.

2. Material and methods

A ^{14}C sampler (Fig. 1) was developed to determine the chemical forms of ^{14}C in the airborne releases of nuclear installations. The sampler allows to simultaneously collect inorganic ($^{14}CO_2$) and organic (^{14}C hydrocarbons) radiocarbon.

The sampler was connected to the standard air ventilation control system at INM. An aerosol filter was installed at the entrance to avoid the contribution of other beta emitters. Air flow rate was 0.5–0.6 l/min. The first bubbler filled with 100 ml of distilled water collected HTO and two following bubblers with 2.5 M NaOH solution captured $^{14}CO_2$. The catalyst (Fig. 2) allowed to oxidize ^{14}CO and ^{14}C-hydrocarbons to $^{14}CO_2$. The following temperature conditions of the catalyst were studied: 400, 550 and 700 °C, for each temperature 2–3 samples were collected. Sampling of each ^{14}C specimen took around one week.

The air mixture is fed through the central hole from the copper coil and enters the preheating layer, consisting of quartz sand (1–2 mm). Further, the already heated gas enters the industrial high-temperature Cr_2O_3/Al_2O_3 alumina catalyst (550–700 °C) [10], where the main part of the reagents is oxidized. Macroporous Al_2O_3 is added above the industrial catalyst layer for better heat transfer from the reactor walls to the gas. For additional oxidation of the reagents in the moderate temperature zone (250–400 °C), Cr_2O_3/SiO_2 catalyst is placed following in the direction of the reagents. The gas then enters the macroporous acid catalyst Cr_2O_3/Al_2O_3 for the next afterburning stage. The final output layer consists of a Pt/Al_2O_3 catalyst for post-oxidation of trace amounts of CO and H_2 in the low-temperature region (100–250°C) [11]. From where, through the outlet displaced relative to the center (indicated by a blue arrow), the gas leaves the reactor to the copper heat exchange coil.

To regulate the heating of the reactor, two spiral heating zones are provided from a winding of insulated 0.5 mm nichrome wire. Each zone has 86-Ohm resistance and is rated at 300 W. Temperature control is carried out automatically through a thermocouple installed in the areas of the highest temperatures of the reactor.

After the sampling 7 ml aliquot from each bubbler were added to 20 ml glass vial with 13 ml of Optiphase HiSafe 3 liquid scintillator. The ^{14}C activity concentration of the prepared sample was then measured using a liquid scintillation counter Quantulus-1220 with measurement time of 60 min [12].

3. Results and discussion

Sampling of gaseous ^{14}C was carried out from November 11, 2021, to March 11, 2022. A total amount of taken samples is 8: three with catalyst temperature 700 °C, three with 550 °C, and two with 400 °C. The results of measuring ^{14}C concentration are presented in Fig. 3.

The concentration excess of organic ^{14}C and ^{14}CO over $^{14}CO_2$ is observed in 3 samples out of 8. In other samples, organic share also makes a significant contribution into the ^{14}C concentration. The share of organic and inorganic ^{14}C is combined in Table 3.

The average contribution of organic species to the ^{14}C concentration depends on the catalyst temperature (mean ± SE, SE means standard error): 36 ± 6 % for 400 °C, 49 ± 18 % for 550 °C and 66 ± 16 % for 700 °C. There is a noticeable trend towards an increase in the proportion with increasing temperature. The difference in the

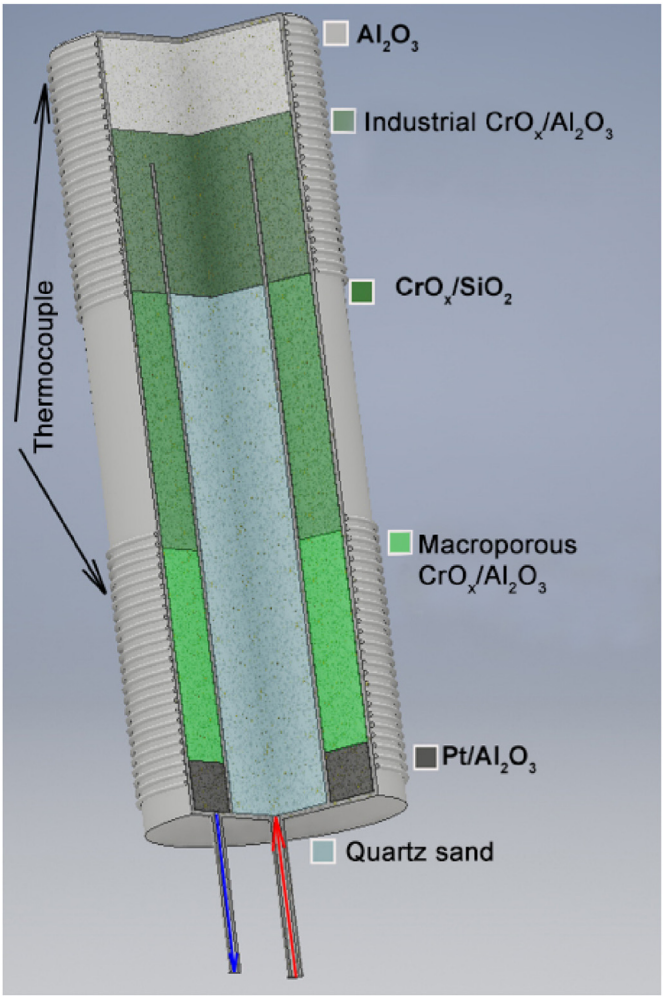

Fig. 2. Scheme of catalyst.

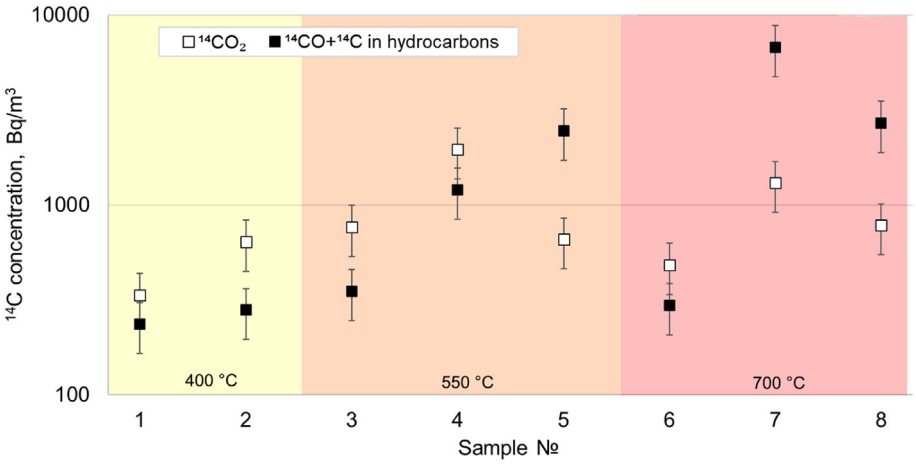

Fig. 3. ^{14}C concentration in samples. Whiskers denote total error in concentration estimation.

Table 3
The share of ^{14}C species in the discharges of INM JSC.

Sample N№	Sampling date	Catalyst temperature, °C	$^{14}CO_2$ share	^{14}CO,$^{14}C_{org}$ share
1	25 Feb – 4 Mar 2022	400	0.59	0.41
2	4–11 Mar 2022	400	0.70	0.30
3	11–19 Nov 2021	550	0.69	0.31
4	22–29 Nov 2021	550	0.62	0.38
5	21–25 Jan 2022	550	0.21	0.79
6	2–9 Feb 2022	700	0.62	0.38
7	10–15 Feb 2022	700	0.16	0,.84
8	16–24 Feb 2022	700	0.40	0,.60

concentration of ^{14}C during the same temperature of the catalyst can be associated with different modes of operation of the reactor (refueling, reactor shutdown, preventive maintenance), as well as different compositions of the reactor core.

The average concentration of ^{14}C during sampling is 2.5 kBq m^{-3} which corresponds to $2.2 \cdot 10^{12}$ Bq a^{-1}. The effective annual dose was calculated according to IAEA methodology based on following assumptions [13]:

(a) Ingestion of carbon originating from the atmosphere is the primary mode of exposure, and all other pathways of exposure will contribute less than 1% of the total dose;
(b) The ^{14}C released is associated with CO_2 molecules and is subsequently fixed within plant tissues during photosynthesis;
(c) The organic molecules thus formed are transported along with stable ^{12}C through food chains and into the human body.

In our calculations we conservatively assumed that radiocarbon entering the atmosphere is in the form of dioxide and then absorbed by plants during photosynthesis. Accounting for the chemical form of ^{14}C is needed when assessing effective doses from inhalation: dose coefficients are $6.5 \cdot 10^{-12}$ Sv/Bq for CO_2 and $5.8 \cdot 10^{-10}$ Sv/Bq for organic gases. However, since the contribution from this irradiation path is less than 1%, it can be neglected. Effective dose from ^{14}C discharge by INM is about 6.3 μSv a^{-1} while the effective dose from natural ^{14}C is 10–15 μSv a^{-1} [15].

Handling with isotope products is the main source of ^{14}C release to atmosphere. This is confirmed by an analysis of the tree rings in the vicinity of INM [14]. A sharp increase of ^{14}C concentration in 1994–1995 due to the start of commercial production of the isotope is observed.

We suppose that the method of active ^{14}C sampling using NaOH absorbent in combination with a catalyst allows to appropriate assess the activity of ^{14}C in emissions from nuclear reactors. Our investigations have demonstrated, that the organic ^{14}C and ^{14}CO make a significant contribution to the total discharge of radiocarbon from a light water research reactor. Since the majority of Russian NPPs operate VVER-type reactors, a significant part of ^{14}C produced in the coolant to be in the form of organic compounds, due to reducing condition in the presence of excessive hydrogen. This is confirmed by the works of V.P. Rublevsky on the study of ^{14}C discharges at the Novovoronezh, Kola, Balakovo and Kalinin NPPs, where the share of organic carbon varied from 15 to 65% [16]. Therefore, it is important to consider the organic fraction of ^{14}C in discharges of light-water reactors.

4. Conclusions

In this study we investigated the composition and concentration of ^{14}C discharges from the Institute of Nuclear Materials. The application of a chromium oxide and platinum catalysts at different temperatures (400, 550, 700 °C) allowed to sample the organic fraction of ^{14}C. It makes a significant contribution to the activity of ^{14}C airborne releases of research water reactor. The minimum share of organic ^{14}C during the experiment was 0.30, maximum – 0.84. There is a noticeable trend between the catalyst temperature and ^{14}C organic concentration. Likely, elevated temperature allows the more stable organic compounds to be oxidized. The obtained results are in good agreement with data on discharges of European NPPs of the PWR (VVER) type.

Declaration of competing interest

The authors declare that they have no known competing

financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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