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$^{14}CO_2$ AND TOTAL AIRBORNE ^{14}C RELEASES FROM A PWR AND A BWR AT RINGHALS NUCLEAR POWER PLANT MEASURED WITH ACCELERATOR MASS SPECTROMETRY

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"Förhållandet mellan C-14 aktiva kolväten och koldioxid
i skorstensutsläppet från ett kärnkraftverk"

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$^{14}CO_2$ and total airborne ^{14}C releases from a PWR and a BWR at Ringhals nuclear power plant measured with accelerator mass spectrometry

Abstract

The $^{14}CO_2$ and the total airborne ^{14}C releases from two Swedish light-water reactors, the boiling water reactor (BWR) Ringhals 1 and the pressurized water reactor (PWR) Ringhals 4, have been analysed using accelerator mass spectrometry (AMS). Five two-week samples, continuously collected from the stack of each reactor, showed that of the total airborne ^{14}C effluents, on the average 93% for the BWR and 14 % for the PWR were released as $^{14}CO_2$.

1. Introduction

^{14}C is one of the radioactive nuclides which is produced by light-water reactors and released to their surroundings during normal operation. Because of the biological importance of carbon and the long half-life of ^{14}C (5730 years) it is of interest not only to study the amount of released activity, but also the chemical form as it is of importance for the biological processes.

^{14}C is produced in light-water reactors mainly by the nuclear reactions $^{17}O(n,\alpha)^{14}C$ and $^{14}N(n,p)^{14}C$. ^{17}O exists naturally in the fuel, moderator and coolant, while ^{14}N may occur as an impurity in the fuel, moderator, coolant and in structural materials [Da79]. Thus different reactor designs will produce varying amounts of ^{14}C. The major part of the created ^{14}C, which leaves the plant during normal operation, is released in gaseous effluents [Ku85] and originates from the cooling water. In pressurised water reactors (PWR) hydrogen is added to the coolant and therefore the produced radioactive carbon isotope is expected mainly to form hydrocarbons. In boiling water reactors (BWR) ^{14}C tends to form carbon dioxide.

The results of a one-year study of the *total* airborne ^{14}C effluents from two Swedish light-water reactors, one BWR (Forsmark 1) and one PWR (Ringhals 4), have been presented in an earlier report [St93a]. Stack air was continuously collected in two-week periods and the ^{14}C content in the samples was analysed using accelerator mass spectrometry (AMS) [St93b]. The ^{14}C activity concentration in the stack air from the PWR varied between 2 and 1132 Bq/m^3 with a mean value of 200 Bq/m^3, and from the BWR the activity concentration varied between 4 and 146 Bq/m^3 with a mean value of 95 Bq/m^3 according to the measurements. In the PWR the ^{14}C release rate was measured to be 0.27 TBq/GW$_{el}$·year, while the BWR showed a ^{14}C release rate of 0.48 TBq/GW$_{el}$·year.

In this report the $^{14}CO_2$ and the total airborne ^{14}C releases, of one PWR (Ringhals 4) and one BWR (Ringhals 1), have been studied. Five two-week samples, continuously collected from the stack of each reactor, have been analysed using the AMS method.

2. Methods

In order to ensure a continuous air sampling during a specific time period, in this case a fortnight, automatic air samplers were constructed and connected to the stack gas monitoring systems in the reactor buildings [Er92]. The stack gas was sampled in 50 litre air bags of sturdy construction and with inner carbon-free linings (Cali-5-Bond™ bags manufactured by Calibrated Instruments, Inc.).

Before the AMS analysis the carbon compounds must be extracted from the air sample and converted to solid carbon. At first ^{14}C-free carbon dioxide is added to the air samples as a carrier, which results in an increment of the ^{12}C and ^{13}C content of 20-100 times, depending on the expected activity of the sample. The presence of the carrier is necessary to reduce the count rate of ^{14}C in the particle detector of the AMS system. It also protects the ion source from unnecessary contamination of ^{14}C from high-active samples. Another advantage is that it abates the influence from small variations in the CO_2 concentration of the stack air [St93a] on the final result of the AMS analysis. In order to analyse the total ^{14}C activity, the gas and the carrier is drawn through a PdAl- and PtAl-catalyst kept at 600°C, which oxidises all carbon compounds to carbon dioxide [Ku85]. To analyse the $^{14}CO_2$ activity only, this oxidising step is not included. Water vapour is removed by drawing the gas mixture through a tube with Drierite (anhydrous calcium sulphate), prior to the absorption of the carbon dioxide in Ascarite (NaOH on a solid support). The obtained sodium carbonate is acidified in a vacuum system, resulting in re-evolved carbon dioxide. Finally, elemental carbon is produced by reducing the CO_2, mixed with hydrogen gas, over an iron catalyst [Vo84].

The AMS facility [Er92, Sk92] is part of the Lund University 3UDH Pelletron tandem accelerator. Each sample requires a measuring time of about 20 minutes. The activity of the carbon sample is determined by comparing the $^{14}C/^{13}C$-ratio of the sample with that of a standard with known activity (the NBS oxalic acid standard [Stu77]). The absolute activity in 1950 of the oxalic acid standard has been measured by gas proportional counting [Ka64] to be 14.27 ± 0.07 disintegrations per minute per gram carbon (the uncertainty denotes the estimated statistical error). In 1993 this corresponds to an activity of 0.2365 Bq/g_{carbon} [Ka64]. With a known amount of ^{14}C-free CO_2-carrier added to the stack air sample, the concentration of $^{14}CO_2$ or total ^{14}C in the stack air can be calculated from

the activity of the carbon sample. Samples of ^{14}C-free anthracite, processed in the sample preparation system, are also measured to provide the background of the sample preparation and accelerator systems.

3. Results and discussion

Table 1 shows the measured ^{14}C activity concentrations of five two-week samples from Ringhals 1 and five from Ringhals 4. The mean values for the total ^{14}C activity concentrations are 90 Bq/m^3 for Ringhals 1 and 167 Bq/m^3 for Ringhals 4.

To check the reproducibility of the sample preparation and measuring procedures, three of the samples were processed and measured at two different occasions. The results agreed within 3 %. This corresponds to the measured accuracy of other types of carbonate samples, processed directly from carbonate to solid carbon. The total error of the measured activity concentrations is estimated to be ±5%, giving an error in the measured fraction of CO_2 of ±7%. Beside the error of 3 % introduced by the production of solid carbon from the sodium carbonate and by the AMS-measurement, an error of 1% is introduced from uncertainties in measuring the volumes and pressures of the gas sample and the ^{14}C-free CO_2-carrier, 1 % may come from possible cross contamination and the efficiency of the catalyst is estimated to give a maximum error of 4%.

Reactor	Period	$^{14}CO_2$-conc. (Bq/m^3)	Total ^{14}C-conc. (Bq/m^3)	Measured fraction $^{14}CO_2$ (%)	Mean fraction $^{14}CO_2$ (%)
Ringhals 1 (BWR)	931115-931124	69±3	72±4	96±7	
	931126-931210	91±5	109±5	83±6	
	931210-931227	98±5	95±5	103±7	
	940131-940214	92±5	91±5	101±7	
	941214-940228	68±3	83±4	82±6	93±4*
Ringhals 4 (PWR)	931101-931115	22±1	147±7	15±1	
	931115-931129	23±1	150±8	15±1	
	931129-931213	25±1	183±9	14±1	
	931213-931227	21±1	160±8	13±1	
	931227-940110	24±1	196±10	12±1	14±1*

Table 1. *The results of the measurements of $^{14}CO_2$ concentrations and the total ^{14}C concentrations in the stack air of the two reactors. * denotes standard error of the mean.*

The measuring period for both the PWR and the BWR were during normal operation, not including any reactor outage. The mean fractions of

$^{14}CO_2$, 93±4 % for the BWR and 14±1 % for the PWR, seem to be in agreement with expected values, according to other measurements.

Table 2 shows a comparison of ^{14}C discharges from pressurized water reactors. These are mean values and perhaps include reactor outages. The outage periods seem to be of great importance for the chemical composition of the ^{14}C releases for PWRs. These periods should therefore not be included in a comparison with the results presented in this report. In a report by Kunz [Ku85], concerning the American PWR Indian Point No. 3, three outage periods are included. The measured fraction of $^{14}CO_2$ varies between about 25% and 100% during these periods, whereas the $^{14}CO_2$ fraction for periods of normal operation varies between about 4 % and 26% with a mean value of about 9 % (excluding the samples taken just after the outages). From this report it is also clear that the total activity as well as the $^{14}CO_2$ fraction released to a great extent depends on the venting of the gas decay tanks and the reactor containment. In a six year study of four Soviet PWRs, each with a capacity of 440 MW_e, at Paks in Hungary, Veres et al [Ve94] reports an average $^{14}CO_2$ fraction of 6 %. The variations in the $^{14}CO_2$ fraction seem to be small, which is probably due to the configuration of the reactor block where two reactors are using the same stack, and where outage periods, plant venting and releases from gas decay tanks are not accounted for.

Reactor	Discharge period	Release (GBq y^{-1})	Normalized release (TBqGW$e^{-1}y^{-1}$)	Chemical form (%) CO_2	C_nH_m	Reference
Biblis A	1977	178	-	8	92	[UN82]
	1978	78	0.07	30	70	[Wi84]
	1976-1977	-	0.04	6	94	[Sc77]
	1983	(41)	-	-	-	[Wi85]
Biblis B	1977	181	-	2	98	[UN82]
	1978	168	0.13	10	90	[Wi84]
	1976-1977	-	0.41	1	99	[Sc77]
	1983	(22)	-	-	-	[Wi85]
Obrigheim	1977	111	-	14	86	[UN82]
	1978	33	-	58	42	[UN82]
	1976-1977	-	0.12	30	70	[Sc77]
	1980	(22)	-	-	-	[UNE89]
	1983	(40)	-	-	-	[Wi85]
Stade	1977	111	-	100	0	[UN82]
	1978	55	-	100	0	[UN82]
	1976-1977	-	0.15	40	60	[Sc77]
	1980	(129)	-	-	-	[UNE89]
	1983	(130)	-	-	-	[Wi85]
Neckarwestheim	1977	148	-	3	97	[UN82]
	1978	144	-	4	96	[UN82]
	1976-1977	-	0.07	30	70	[Sc77]
	1980	(110)	-	-	-	[UNE89]
	1983	(26)	-	-	-	[Wi85]
Unterweser	1980	(26)	-	-	-	[UNE89]
	1983	(22)	-	-	-	[Wi85]
FRG PWRs mean	1978-1981	-	0.21	-	-	[Wi84]
Five FRG PWRs	-	-	0.22	20	80	[Sc77]
R.E. Ginna	1980-1981	-	0.43	10	90	[Wi85]
Indian Point	1980-1981	-	0.36	26	74	[Ku85]
PWR "A" (US)	-	-	0.37	19	90	[Wa78a]
European	-	-	0.22	-	-	[UN82]
PWRs mean	-	-	0.37	-	-	[UN82]
USSR PWR type	-	-	0.95-10.6	-	-	[Ru87]
Paks, Hungary	1988-1993	-	0.80	6	94	[Ve94]
Ringhals 4	1991-1992	-	0.27	-	-	[St93a]

Table 2. *^{14}C discharges from pressurized water reactors. Data in parenthesis refer to CO_2 form, only, and -=no data. Data except the values from Paks and Ringhals are taken from Uchrin et al [Uc92].*

Concerning the releases from BWRs, Wahlen & Kunz [Wa78b] reports that over 95 % of the ^{14}C activity in off-gas samples of six BWRs was in the form of $^{14}CO_2$. In another study by Kunz [Ku85], eight off-gas grab samples from the BWR James A. Fitzpatrick showed an average ^{14}C composition of 95 % $^{14}CO_2$ and 5 % hydrocarbon gases. According to a literature survey by Snellman [Sn88] similar results were obtained at four BWRs in the Federal Republic of Germany ([Wi84, Sc78]).

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