IDENTIFICATION AND FORMATION OF CARBON-14 CONTAINING ORGANIC COMPOUNDS DURING ANOXIC CORROSION OF ACTIVATED STEEL IN ALKALINE CONDITIONS

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Carbon-14 is an important radionuclide in the inventory of radioactive waste. In Switzerland, the ^{14}C inventory in a cement-based repository for low- and intermediate-level radioactive waste (L/ILW) is mainly associated with activated steel (~85 %). In light water reactors (LWR) ^{14}C is the product of ^{14}N activation in steel parts exposed to thermal neutron flux. ^{14}C has been identified a key radionuclide in safety assessments. Release of ^{14}C occurs due to slow corrosion of activated steel in the near field of a deep geological repository. While the ^{14}C inventory is well known, the speciation of ^{14}C upon release from activated steel is only poorly understood. The present study is aimed at investigating the formation of carbon species during the anoxic corrosion of iron and steel and determining the ^{14}C species formed in a corrosion experiment with activated steel. The experiments were carried out in conditions similar to those anticipated in the near field of a cement-based repository.

I. INTRODUCTION

Carbon-14 is an important radionuclide in the inventory of radioactive waste[1,2] and it has been identified a key radionuclide in safety assessments due its long half-life (5730 y)[3,4]. ^{14}C is of specific concern due to its potential presence as either dissolved or gaseous species in the disposal facility and the host rock, the high mobility of dissolved carbon compounds in the geosphere caused by weak interaction with mineral surfaces in near neutral conditions, and eventually because it can be incorporated in the human food chain. Current safety assessments are based on specific assumptions regarding the rate of release from potential sources, the speciation upon release and the mobility of the different forms of carbon in the cementitious near field[1].

The main source of ^{14}C in low- and intermediate-level radioactive waste in Switzerland are activated metallic nuclear fuel components and reactor core components as well as spent filters and ion exchange resins used in the LWRs for the removal of radioactive contaminants in a number of liquid processes and waste streams. Compilations of the activity inventories reveal that in the already existing and future arisings of radioactive waste in Switzerland, the ^{14}C inventory is mainly associated with activated (or irradiated, respectively) steel (~85 %) while the ^{14}C inventories associated with nuclear fuel components (e.g. Zircaloy) and waste from the treatment of reactor coolants (e.g. spent ion exchange resins) are much smaller. ^{14}C in activated steel results mainly from ^{14}N activation ($^{14}N(n,p)^{14}C$)[2]. Release of ^{14}C occurs during corrosion of activated steel in the cementitious near field. A recent review of corrosion rates suggests that steel corrosion in these conditions is a very slow process[5,6].

Carbon-14 can be released in a variety of organic and inorganic chemical forms. ^{14}C will decay within a disposal facility if the ^{14}C-bearing compounds are retained by interaction with the materials of the engineered barrier. Inorganic carbon, i.e. $^{14}CO_2$ (and its bases), is expected to precipitate as calcium carbonate within a cement-based repository or undergo $^{14}CO_3^{2-}$ isotopic exchange with solid calcium carbonate. Therefore, inorganic ^{14}C has only a negligible impact on dose release. By contrast, gaseous species containing ^{14}C, such as $^{14}CH_4$ and ^{14}CO, could form and migrate with bulk gas from the near field into the host rock. Previous studies indicate that a limited number of small organic molecules are likely to be formed in the course of the anoxic corrosion of activated steel in alkaline conditions[7]. More specifically, reduced hydrocarbons, such as methane, ethane etc., and oxidized hydrocarbons, such as alcohols, aldehydes and carboxylic acids were detected in these conditions. Thus, both oxidized and reduced hydrocarbons have been observed in iron-water systems in anoxic (near neutral to alkaline) conditions which seems to be inconsistent with a view to the negative redox potential determined in anoxic iron-water systems[8].

Although the ^{14}C inventory associated with activated steel is well known, our understanding of the chemical form of the ^{14}C-bearing compounds produced in the course of the anoxic corrosion of activated steel is limited. The present study is aimed to fill this knowledge gap.

II. CORROSION EXPERIMENT WITH ACTIVATED STEEL

The project aims at identifying and quantifying the ^{14}C-bearing species formed in a corrosion experiment with activated steel. Five irradiated steel nuts were received from the nuclear power plant (NPP) Gösgen, Switzerland. The material has a high dose rate (~100 mSv/h contact dose rate of each steel nut)[9]. Major limitations had to be taken into consideration when planning the corrosion experiment: 1) only a small amount of activated steel can be used in a corrosion experiment outside a hot cell due to the high dose rate of the material, and 2) the corrosion rate of stainless steel in alkaline conditions is very low (typically < 10 nm/a)[5,6]. Taking into account these limitations the resulting concentration of the ^{14}C-bearing compounds produced over an experimental period up to few years is well below the detection limit of classical radio-analytical methods for ^{14}C determination, in particular liquid scintillation counting (LSC). Scoping calculations further revealed that accurate detection of these compounds required the development of a very sensitive analytical method suitable to quantify ^{14}C-bearing compounds on an activity level in the range of a few µBq. ^{14}C accelerator mass spectrometry (AMS) is the most sensitive technique capable of detecting ^{14}C and in combination with chromatographic separation of the individual ^{14}C-bearing compounds (this combination is denoted as compound-specific ^{14}C AMS), it was expected to allow ^{14}C-bearing compounds to be identified and quantified at the required activity level. In view of this challenging task it was decided to divide the project into several sub-tasks: i) identification and quantification of the organic compounds produced during the anoxic corrosion of iron and steel, ii) characterization of the activated steel used in the corrosion experiment, iii) development of a compound-specific ^{14}C AMS method for the detection of gaseous and dissolved ^{14}C-bearing compounds at very low ^{14}C concentrations, iv) set-up and sampling of a corrosion experiment with activated steel. A schematic presentation of the experimental design is shown in Fig. 1.

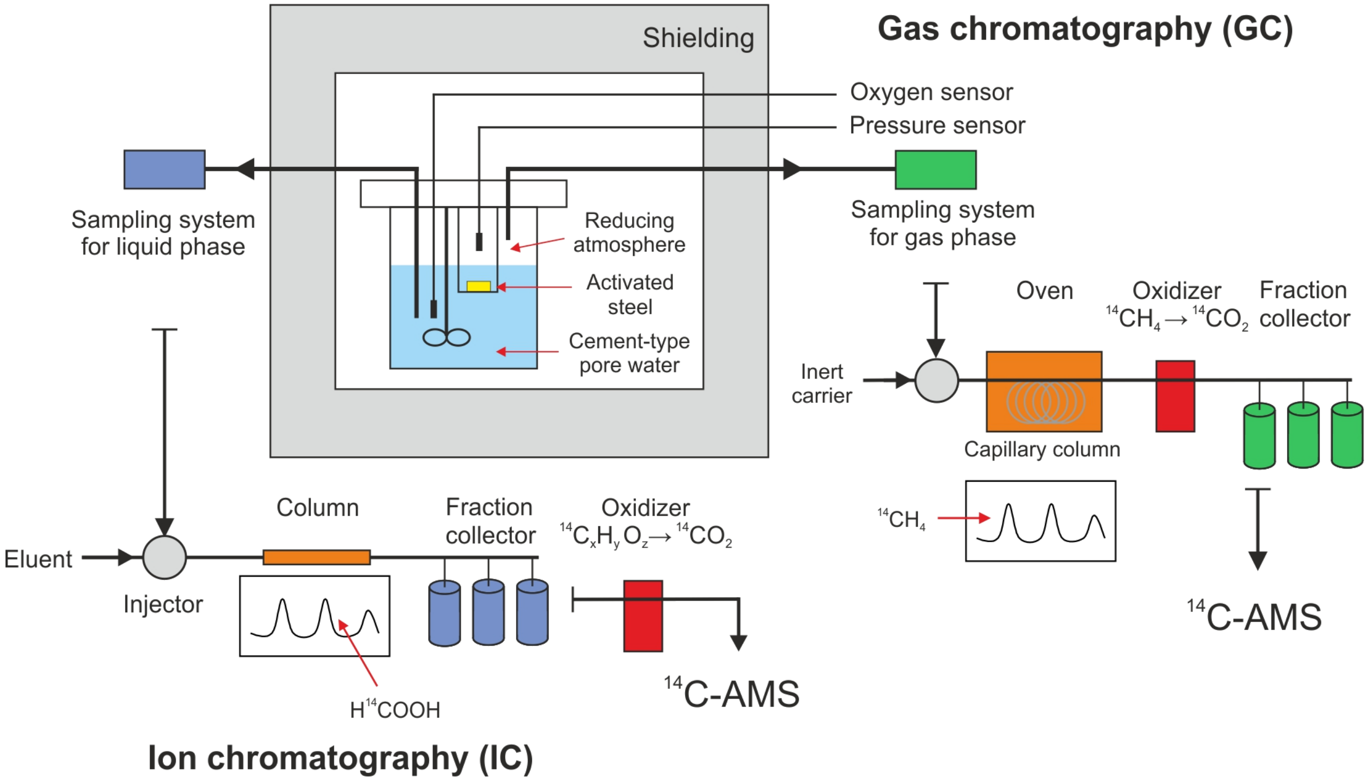

Fig 1. Schematic presentation of the design of the corrosion experiment with activated steel. Reactor set-up for the corrosion experiment with activated steel (top); analytical procedures for the detection of ^{14}C-bearing dissolved organic compounds (bottom) and gaseous species (right).

II.A. Identification of organic corrosion products

A literature survey disclosed the inconsistency in the nature of organic compounds determined in corrosion experiments with iron and steel in anoxic alkaline conditions[7]: Both oxidized and reduced compounds had been identified while the redox potential of the iron-water system is < - 0.6 V, thus promoting the formation of reduced carbon species[8]. We carried out a series of batch-type corrosion experiments with non-activated iron powders with the aim of checking the carbon speciation in these conditions[10]. Detailed knowledge of the speciation is required for the development of the compound-specific ^{14}C AMS method (see Section II.C.). Untreated iron powder and iron powder pretreated by an acid wash were immersed in alkaline solution (artificial cement pore waters (ACW) with pH 13.3, 12.5 and 11.5) and equilibrated over a time period of about 1 month. The organic compounds present in the liquid and gas phase were identified by high performance ion exchange chromatography (HPIEC) with mass spectrometry (MS) detection and gas chromatography (GC) with MS detection. It was observed[10] that only a limited number of compounds are generated during iron corrosion (Table I), i.e. dissolved and volatile low molecular weight (LMW) organics up to C5.

TABLE I. Carbon species released in the course of iron corrosion.

Alkane/alkene	**Alcohols/aldehydes**	**Carboxylic acids**	**Carbonate**
Methane (CH_4)	Methanol (CH_3OH)	Formate ($HCOO^-$) (FA)	CO_2
Ethane (C_2H_6)	Ethanol (C_2H_5OH)	Acetate (CH_3COO^-) (AA)	CO_3^{2-}
Ethene (C_2H_4)	Formaldehyde (CH_2O)	Propanoate ($C_2H_5COO^-$)	(CO)
Propane (C_3H_8)	Acetaldehyde (C_2H_4O)	Butanoate ($C_3H_7COO^-$)	
Propene (C_3H_6)		Malonate ($CH_2(COO^-)_2$) (MA)	
Butane (C_4H_{10})		Oxalate ($C_2O_4^{2-}$) (OA)	

II.B. Characterization of activated steel

Five activated fuel assembly guide tube nuts made of stainless steel were retrieved from the cooling pond for nuclear fuel elements of the NPP Gösgen and transported to the hot laboratory of the Paul Scherrer Institute. The nuts had been positioned at the bottom end of fuel rods and exposed to thermal neutron flux for ~2 years. Each nut (Fig. 2) had a weight of ~5 g (diameter: 1 cm; height: 1.1 cm) and a contact dose ratio of ~100 mSv/h. Two nuts were processed to prepare ten small specimens for laboratory experiments (Fig. 2). The ^{14}C content of three activated steel specimens was determined using a wet chemistry digestion method and LSC for the ^{14}C activity measurements[9]. The method is based on a stepwise dissolution process using a mixture of concentrated HCl and HNO_3 heated to boiling point in the first step, and a mixture of boiling concentrated sulfuric, perchloric and nitric acid in the second dissolution step. Carbon bonded in the activated steel was released as CO_2 and collected in two traps containing 1 M NaOH solution. The ^{14}C activity in aliquots taken from the NaOH solutions was determined by LSC. A standard steel sample with certified carbon content (0.864 %) was used to test and check the method. The results showed that in the activated steel a large portion of ^{14}C was released in the first dissolution step (~90 %) and only a small portion remained in the graphitic residue (~10 %). The total ^{14}C inventory from three replicates was determined to be 17.8 ± 2.5 kBq g^{-1}, indicating that the ^{14}C inventory in the activated steel is very low.

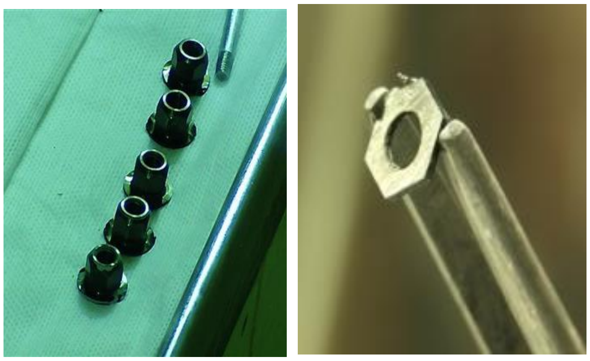

Fig. 2. Activated steel nuts obtained from NPP Gösgen (left); specimens prepared from a steel nut (right).

II.C. Development of compound-specific ^{14}C AMS

Carbon-14 AMS is the only suitable technique capable of detecting very low ^{14}C activities. Dealing with such low activities, however, bears the risk of potential contamination effects as ^{14}C is also a naturally occurring radionuclide produced in the upper atmosphere in the form of $^{14}CO_2$ (activity of 1 m^3 air ~ 53 mBq). Alkaline solutions are a commonly known sink for CO_2 and thus for $^{14}CO_2$. Therefore, the ^{14}C background in the corrosion experiment with activated steel could be affected by an undesirable uptake of ^{14}C from the atmosphere in any stage of sample preparation and handling. The average ^{14}C background was determined to be $F^{14}C = 0.06 \pm 0.02$ ($F^{14}C$ = fraction modern) in the samples after ion chromatographic (IC) separation and using pre-cleaned plastic vials for injection and collection. This finding indicates that the proposed analytical approach is viable.

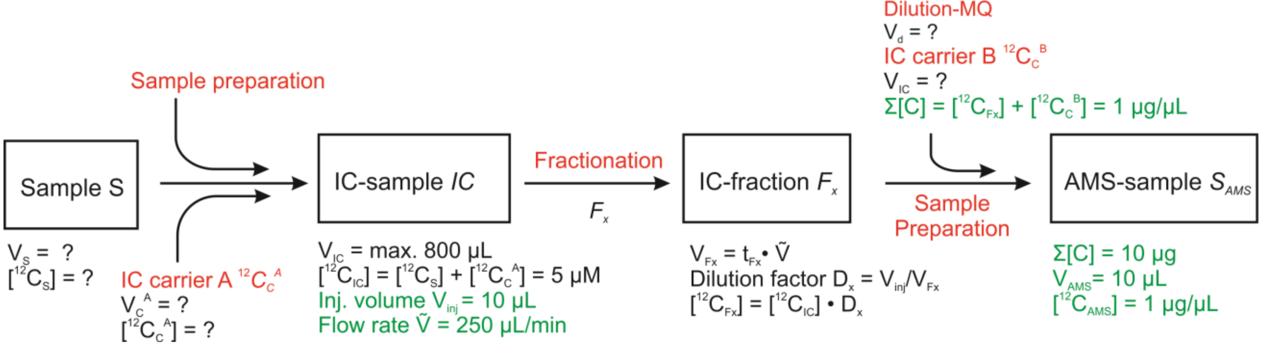

Fig. 3. Flow chart of sample preparation for compound-specific ^{14}C AMS.

Sample preparation for compound-specific ^{14}C AMS method required the various dilution processes during chromatographic separation of single compounds to be considered adequately with the aim of reaching the target dynamic range of the AMS (Fig. 3). Dilution of the samples by a factor 1:25 and 1:50 occurred in the course of chromatographic separation. Measurements with ^{14}C-labelled carboxylic acids showed that the dynamic range of the facility covers $F^{14}C$ values between ~0.06 - ~50.

Recovery of the compound-specific ^{14}C AMS method was determined using four different ^{14}C-labelled carboxylic acids (^{14}C-AA, ^{14}C-FA, ^{14}C-MA and ^{14}C-OA; see Table I) dissolved in either deionized, decarbonated water (ultrapure water generated by Millipore Gradient A10 water purification system) or in ACW (pH 12.5). The samples were sequentially injected into the IC system as single compounds. The corresponding fractions of the ^{14}C-labelled carboxylic acids were collected and analyzed by AMS[11]. Recoveries (%) were determined for each compound and for mixtures of the compounds taking into account the dilution factor during IC separation and fractionation. The recoveries were determined to be 97 ± 17 %[12].

The corrosion studies with non-activated iron powders revealed that gaseous organic compounds are formed during iron corrosion (Table I). This finding implies that the development of a compound-specific ^{14}C AMS analytical method for ^{14}C-bearing gaseous species is required. The analytical approach for the detection of ^{14}C-bearing gaseous (alkane, alkene) and volatile (alcohols, aldehydes) compounds is similar to that previously elaborated for dissolved compounds (carboxylic acids) and will be based on gas chromatographic (GC) separation in combination with ^{14}C detection by AMS. To this end, the GC system has to be coupled to a combustion reactor and a fraction sampling system for $^{14}CO_2$. At present, in-house development of this previously not reported method for compound-specific ^{14}C AMS of gaseous and volatile compounds is ongoing.

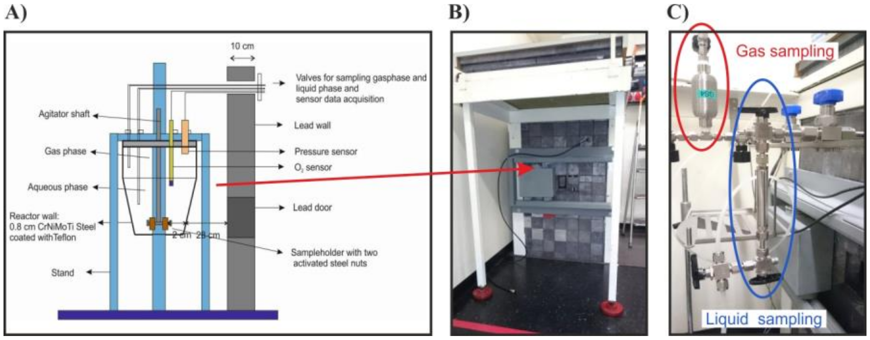

Fig. 4. A) Sketch of the reactor, B) picture of the lead shielding with door and C) the sampling system for liquid and gaseous samples placed outside of the shielding.

II.D. Set-up of the corrosion experiment with activated steel

The experimental set-up for the long-term corrosion experiment with the activated steel nuts consists of a custom-made gas-tight overpressure reactor placed within a 10 cm thick lead shielding (Fig. 4). The reactor has a total volume of 500 mL. For the experiments two activated steel segments of ~1 g (Fig. 4) were immersed in 300 mL ACW (pH 12.5) in a N_2 atmosphere (200 mL). The reactor is equipped with a digital pressure transmitter, a temperature sensor and a sensor to detect dissolved oxygen (Visiferm DO Arc, Hamilton, USA). The overpressure reactor is designed in such a way that all manipulations necessary for regular sampling can be carried out outside the lead shielding to minimize exposure of the experimentalist to radiation. Leak tests confirmed gas-tightness of the reactor. The corrosion experiment with activated steel was started in May 2016. The results from the first few samplings (Table II) show that the activity of total organic ^{14}C increases with time, thus indicating progressing corrosion. At the present time, however, identification and quantification of the individual ^{14}C organic compounds by compound-specific ^{14}C AMS is not possible as their concentration is below the detection limit of the method. Also, the concentration of the ^{12}C + ^{14}C compounds listed in Table II, i.e. hydrocarbons and carboxylic acids, is still below or close to the detection limits of GC-MS and IC-MS, respectively. Note that the latter analytical techniques allow stable plus ^{14}C-bearing carbon species to be identified and quantified as activated steel contains ^{12}C as an interstitial alloying constituent in addition to ^{14}C produced in the course of ^{14}N activation ($^{14}N(n,p)^{14}C$). Thus, the production of all organic compounds formed during the course of the corrosion process is monitored which will enable us to estimate the ratio of ratio of ^{12}C to ^{14}C species.

TABLE II. Carbon species expected to be formed as a result of iron/steel corrosion

Time	O_2	Pressure	Total dissolved ^{14}C AMS		TOC	Hydrocarbons [µM]			Carboxylic acids [µM]				
[d]	[ppb]	[bar]	[$F^{14}C$]	[Bq/L]	[ppm]	Methane	Ethane	Ethene	Formate	Acetate	Oxalate	Glycolate	Lactate
0	58.84	5.03	0.59	0.27	-	-	-	-	< 5	n.d.	< 0.1	n.d.	n.d.
1	43.22	5.15	0.69	0.31	-	n.d.	n.d.	n.d.	7	n.d.	0.3	0.4	n.d.
15	38.86	5.02	1.58	0.71	2.31	n.d.	n.d.	n.d.	8	n.d.	0.5	1.3	1.5
29	37.52	5.04	2.15	0.97	2.41	n.d.	n.d.	n.d.	7	n.d.	0.4	1.3	1.1
93	43.20	5.06	4.12	1.86	4.23	0.13	n.d.	n.d.	11	n.d.	0.6	1.6	2.5

III. SUMMARY AND CONCLUSIONS

Our current understanding of the type of ^{14}C-bearing species produced during anoxic corrosion of activated metals is very limited. This information, however, is required with the aim of improving safety assessment of nuclear waste repositories containing activated metals (e.g. activated steel, Zircaloy) as waste materials. A unique corrosion experiment with activated steel from NPP Gösgen, Switzerland, is currently being carried out with the aim of identifying and quantifying the ^{14}C-bearing carbon species produced in the course of the corrosion process under hyper-alkaline, anoxic conditions. As the concentrations of these species is expected to be very low, a specific analytical technique was developed by combining chromatographic separation of individual compounds with ^{14}C detection by AMS (compound-specific ^{14}C AMS). The method is characterized by a low detection limit and a large dynamic range (~3 orders of a magnitude) and therefore it is well suited for application in the corrosion experiment with activated steel. The method was developed for selected, potentially ^{14}C-bearing compounds of interest as previous studies with iron indicated that only a limited number of carbon species are being formed during corrosion. The specific set-up developed for the corrosion experiment allows continuous monitoring of important physico-chemical parameters (pressure, temperature, dissolved oxygen) and further allows aliquots of liquid and gas to be sampled from the reactor outside the lead shielding. Analysis of the liquid and gas phase from the first sampling campaigns show that the concentrations of the organic compounds (^{12}C- and ^{14}C-bearing) are still very low, i.e. below or close to the detection limit of the analytical methods used in this study. Nevertheless, measurement of the total ^{14}C concentration of the samples indicates progressing corrosion with time which suggests that the carbon-containing corrosion products might be detectable in future samples. Thus, we conclude that the present set-up of the experiment is well suited to explore corrosion of activated metals.

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