CORROSION OF IRRADIATED STEEL IN CEMENTITIOUS ENVIRONMENT: SPECIATION OF CARBON-14

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Introduction

^{14}C has been identified as a major contributor to the long-term activity released from a cement-based waste repository. In Switzerland, this ^{14}C inventory is mostly associated with irradiated steel (~75%).

The chemical speciation of the ^{14}C-bearing compounds in the cementitious environment upon release from irradiated steel is still not completely understood (Figure 1).

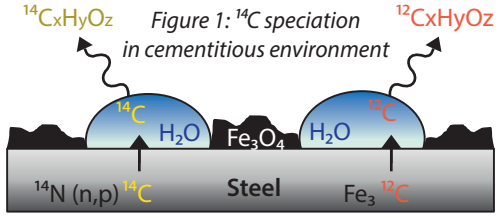
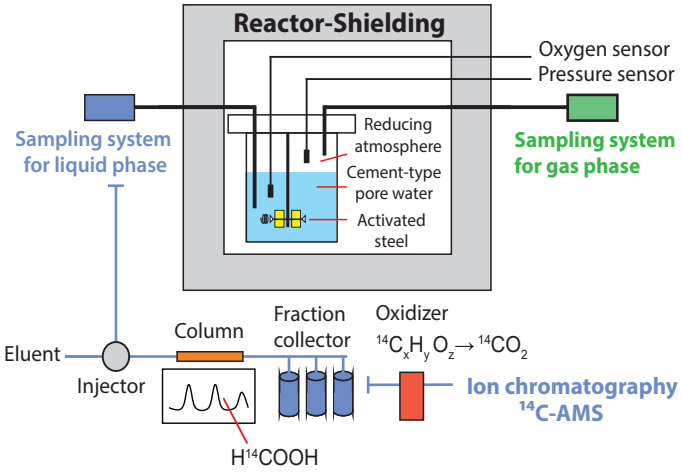


Figure 1: ^{14}C speciation in cementitious environment

The corrosion experiment, developed at PSI since May 2016, allows us a first identification and quantification of the ^{14}C-bearing compounds present in the aqueous phase by using ion chromatography (IC) and an accelerator mass spectrometry (AMS) (Figure 2).

Material & Methods

Figure 2: The corrosion experiment with irradiated steel and the analytical set-up for dissolved compound analyses



Results & Discussion

Formate (FA), acetate (AA) and lactate (LA) are the major components of the total organic ^{14}C in solution (TO^{14}C) (Table 1) [2]. They have been also identified in corrosion studies with non-irradiated iron powders [3].

Table 1: Carboxylates and TO^{14}C concentrations in the aqueous phase.

	Dilution corrected data	
Fraction	M	Error
Formate	1.33E-13	5.28E-14
Acetate	1.02E-13	3.94E-14
Lactate	8.61E-14	3.98E-14
Sum	3.21E-13	1.32E-13
TO^{14}C	2.86E-13	

TO^{14}C first increased with time (up to 92 days), underlying a production of aqueous ^{14}C-bearing organic compound during irradiated steel corrosion. On the long-term, TO^{14}C seemed to slightly decrease (Figure 3a), potentially indicating a decomposition of dissolved compounds [2].

The release of the total ^{14}C to solution was modelled on the assumption that fast corrosion took place in the early phase (20nm/a) followed by a slower corrosion in the long term (2nm/a) (Figure 3a). While these two corrosion rates are both consistent with the one of stainless steel in hyper-alkaline environment and based on the fact that the total amount of ^{14}C released is present in the dissolved organic chemical form (TO^{14}C), 20nm/a and 2nm/a are considered to be lower limits [2].

The modelling results indicated that the concentrations of dissolved stable carbon-bearing compounds (TO^{12}C) obtained by experiments were significantly higher than the modelled concentrations (Figure 3b). This could be explain by two hypothesis: ^{14}C and ^{12}C were released by very different kinetics or an additional unknown carbon source contributed to the production of TO^{12}C.

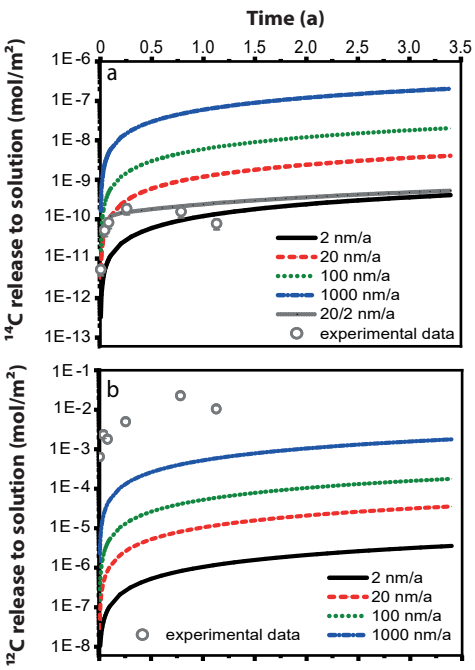


Figure 3: Modelling of a) the total ^{14}C and b) ^{12}C concentrations in the liquid phase as function of corrosion rates.

Conclusion and Outlooks

A compound specific radiocarbon analysis was successfully developed, allowing the quantification and modelling of extremely low concentrations of ^{14}C-bearing carboxylates released in alkaline solution during irradiated steel corrosion.

Further samplings and investigations will be conducted in order to see if a TO^{14}C decomposition occurs with time and to understand the production of TO^{12}C. Moreover, a new method combining gas chromatography and AMS will be developped to identify and quantify gaseous compounds released during the anoxic corrosion of irradiated steel (Figure 4).

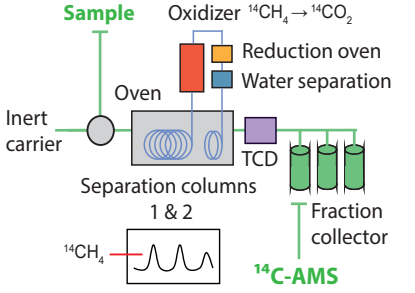


Figure 4: The sampling and analysis of the gaseous phase.

References

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