Release of carbon from metallic waste in disposal conditions

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INTRODUCTION

Radiocarbon, C-14, is a major radiotoxicity contribute in decommissioning waste with half-life of 5,730 years. Because of its chemistry, it may release either in inorganic or organic form. Especially organic species can be highly mobile in geosphere and migrate to the biosphere.

In this project the aim was to develop understanding of the release mechanism and rate of the release of carbon-14 from the activated metallic waste materials in geological disposal conditions.

The project was also involved in the CAST (CArbon-14 Source Term) EU project (WP: Steels) which started in 2013 and ended in March 2018.

MATERIALS

In order to select relevant conditions with respect to the final disposal of decommissioning waste in Finland, leaching solutions were prepared based on the composition of natural groundwater samples from Loviisa site. Two pH values were chosen, pH 12.5 simulates the effect of cement in the repository conditions and pH 8.5 was selected as reference.

Table 1. *Sample information.*

Sample	Irradiated	Activity (^{60}Co MBq)	C, N (w%)
Mod.AISI316Ti	No	-	0.3 (carbide), 0,1
Fe_3C	No	-	6.3 (interstitial atom), -
Surveillance capsule material	Yes	Sample A, 227.27 Sample B, 619.23	0.023, 0.040

The speciation of ^{14}C in irradiated steel, arising from the activation reaction of nitrogen, is not known sufficiently well. It has been suggested to be present as carbide or interstitial atoms in the austenitic steel lattice. Therefore, the non-irradiated materials chosen for the experiments were AISI316Ti type stainless steel and Fe(III)carbide (Fe_3C). The steel powder was manufactured and modified at VTT 'Material modelling and eco-design' team. The composition and microstructure, including the form of C, were verified with the SEM, EDS and optical microscopy analyses. The irradiated samples were cut from the surveillance capsule chain originated from Loviisa nuclear reactor. On the basis of the initial N content and the irradiation history, the theoretical maximum content of ^{14}C after exposure was calculated to be 2 x 10^3 Bq ^{14}C/g (Table 1).

EXPERIMENTAL SET-UP

The leaching experiments with non-irradiated materials were started in 2015. The elution of carbon to both gas and liquid phases was investigated under anaerobic conditions in the glove box (Ar).

The two specimens cut from the capsule chain were immersed into the leaching solutions (two separated vessels) in June 2016 inside an under pressure glove box behind a lead shield at room temperature. In this experiment the sampling was performed only from the liquid phases (Figure 1).

Figure 1. *Experimental set-ups.*

RESULTS

In all the experiments majority of the carbon was released in organic form to liquid phase. The results of DIC/DOC analysis are presented in Figure 2.

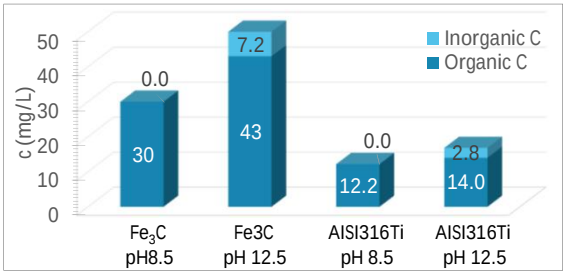

Figure 2. *Distribution between organic and inorganic carbon.*

The carbon release rates were calculated to be: $1.7x10^{-4}$ –$3.1x10^{-4}$ for Fe_3C and one order in magnitude less for modified AISI316Ti. The composition of organic compounds in the liquid phase was analysed by gas and liquid chromatography connected to mass spectrometry. The volatile organic alcohols detected were methanol, ethanol and 1-propanol. In gas phase small hydrocarbons were detected in Fe_3C samples as well as high concentrations of CO (1100-190ppm). No organic or inorganic carbon compounds were detected in AISI316Ti samples.

The beta and gamma activities of the samples from the irradiated experiments were determined without any pre-treatment of the solutions. Clearly higher activities were detected in lower pH (8.5) leaching solution experiment.

Conclusions

- **It seemed that virtually all carbon was released in organic form into liquid phase in experiments with non-irradiated materials.**
- **In gas phase, significant amount of carbon was found in inorganic.**
- **The effect of the original form of C (carbide/ interstitial atom) on speciation in liquid/gas phase remains uncertain.**
- **The experiments with the irradiated material were shorter than originally planned. The results suggested stronger corrosion at the pH of 8.5.**

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