CArbon-14 Source Term

CAST

Release and speciation of carbon from stainless steel under mildly and highly alkaline, reducing conditions (D2.9)

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CAST – Project Overview

The CAST project (CArbon-14 Source Term) aims to develop understanding of the potential release mechanisms of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal to underground geological disposal facilities. The project focuses on the release of carbon-14 as dissolved and gaseous species from irradiated metals (steels, Zircaloys), irradiated graphite and from ion-exchange materials as dissolved and gaseous species.

The CAST consortium brings together 33 partners with a range of skills and competencies in the management of radioactive wastes containing carbon-14, geological disposal research, safety case development and experimental work on gas generation. The consortium consists of national waste management organisations, research institutes, universities and commercial organisations.

The objectives of the CAST project are to gain new scientific understanding of the rate of re-lease of carbon-14 from the corrosion of irradiated steels and Zircaloys and from the leaching of ion-exchange resins and irradiated graphites under geological disposal conditions, its speciation and how these relate to carbon-14 inventory and aqueous conditions. These results will be evaluated in the context of national safety assessments and disseminated to interested stakeholders. The new understanding should be of relevance to national safety assessment stakeholders and will also provide an opportunity for training for early career researchers.

For more information, please visit the CAST website at:
http://www.projectcast.eu

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Release and speciation of carbon from stainless steel under mildly and highly alkaline, reducing conditions

Executive Summary

Carbon-14 is an important radionuclide in safety assessment. It has a half-life of 5,730 years. Because of its chemistry, ^{14}C may be released in inorganic or organic form. The forms of ^{14}C–bearing species define the potential transport pathways that must be considered when assessing the migration of carbon-14 from the engineered system of a geological repository.

The CAST project (Carbon-14 Source Term) aimed to develop understanding of the potential release mechanisms and the rate of release of carbon-14 from radioactive waste materials in geological disposal conditions. We were involved in the Work package 2 (WP2), which was dedicated to steel in the CAST project. Our work focused on the release of carbon-14 (and carbon-12) from irradiated and un-irradiated steel materials as dissolved and gaseous species.

The work was started with unirradiated materials in order to develop the experimental methods and protocols. The experiments were performed inside an anaerobic glove box with iron carbide and modified AISI316Ti steel powders leached with two simulated groundwaters of pH 8.5 and 12.5. The speciation of released carbon was investigated in both aqueous and gaseous phases. The high chloride concentration in the initial leaching solutions disturbed the sensitive speciation analyses and the limit of detection remained too high for accurate results.

The irradiated sample chosen for the experiment came from the surveillance capsule chains from the Loviisa nuclear reactor. The analytical data for the composition of the capsule material (stainless steel) was available and the nitrogen content of the initial, unirradiated material was analysed. From the initial composition and irradiation history, the theoretical maximum ^{14}C content after exposure was calculated to be 2 x 10^3 Bq ^{14}C/g.

The two specimens for ^{14}C leaching experiments were cut from this capsule chain. The ^{60}Co activities for the two specimens were measured to be 227.27 MBq and 619.23 MBq. With the help of a steel wire, the specimens were put in zirconia crucibles (Vol. 175 mL), which were inside of a 500 mL Duran glass bottle. The set-up was placed inside an under pressure glove-box (Ar) behind a lead shield (room temperature, 1 atm). Synthetic groundwater with pH 8.5 and 0.01 M NaOH solution (pH 12) were used as the leaching solutions. In the experiments with irradiated steel specimen only the liquid phase sampling was performed. The results of the analyses in the experiment with irradiated steel suggested stronger corrosion at the lower pH of 8.5.

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1 Introduction

The objective of this study was to investigate the release and speciation of ^{14}C during corrosion of irradiated steel under the disposal conditions of decommissioning waste in a cement-based repository. It is probable that the release rates are very low under anaerobic conditions. However, considerable uncertainty concerning the speciation of ^{14}C exists, especially on the proportion of organic ^{14}C vs. inorganic ^{14}C. Organic species may be highly mobile in geosphere and improved knowledge of the speciation would help to make safety analyses somewhat more realistic. ^{14}C is present after irradiation in stainless steel components of reactors principally as a result of the reaction ^{14}N (n,p) ^{14}C. The chemical state of ^{14}C in irradiated steel is not known with certainty. It has been suggested by Johnson and Schwyn (2004) that ^{14}C arising from nitrogen is present in the form of carbide in various metals or as interstitial atoms in the austenitic steel lattice.

In order to investigate the influence of the initial speciation of carbon, the solid phases chosen for the experiments were unirradiated AISI316Ti type stainless steel and Fe(III)carbide (Fe_3C) powders, in which carbon is in interstitial atom and carbide form respectively. The release and speciation of ^{12}C into the liquid and gaseous phases was studied. The leaching experiments were conducted in synthetic groundwaters. The composition of these waters simulated the composition of natural groundwater samples collected from Loviisa repository site. The pH 12.5 water was used to simulate the effect of cement in the repository conditions. The pH 8.5 worked as reference. All the leaching experiments were conducted under anaerobic conditions.

In the experiments with irradiated steel specimens the objective was to determine the release rate of ^{14}C and whether it is released as an organic or inorganic form into liquid phase. Also the speciation of the released organic carbon compounds was in focus. The samples chosen for the irradiated experiments were cut from a stainless steel capsule, which originated from the surveillance capsule chain irradiated in the Loviisa nuclear reactor. Two irradiated specimens were immersed in leaching solutions in the experimental vessels behind a lead shield inside an under-pressure glove box (Ar). The high activity level of steel samples (227.27 MBq, 619.23 MBq) limited the number of experiments.

2 Materials

2.1 *Leaching solutions*

In order to select relevant conditions with respect to the final disposal of decommissioning waste in Finland, simulated groundwaters were chosen as the leaching solutions for the experiments. Groundwater samples were collected from a borehole (LPVA5) from the Loviisa site and analysed. The compositions of prepared simulant waters are based on the composition of this natural groundwater sample. However, e.g. redox sensitive elements and the elements with low concentration were excluded from the simulant waters. The composition of analysed natural LPVA5 groundwater is presented in Table A1-1 (App.1). The selected composition of the simulant waters were modelled with the geochemical equilibrium codes EQ3 and PHREEQ to ensure the stability of the simulant waters in glove box conditions (Ar atmosphere, O_2 less than 1 ppm and low CO_2). The final compositions of prepared simulant groundwaters are presented in Table 1. The simulant groundwaters were prepared in the glove box from O_2-free milliQ water and chemicals with at least PA grade. 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. Prepared simulant waters were held in the glove box several weeks prior to the beginning of the leaching experiments. The pH was adjusted with NaOH solution and measured several times to ensure the stability of the waters.

Table 1: Composition of simulated groundwaters (mmol/L) based on natural groundwater composition and geochemical modelling. The compositions were modelled for Ar atmosphere with O_2 < 1 ppm and low CO_2.

	CA85	**CA125**
pH	*8.5*	*12.5*
Na^+	117	168
Ca^{2+}	16	15
K^+	0.6	0.6
SO_4^{2-}	5.8	5.8
Cl^-	137	137
Br^-	0.2	0.2

These two simulated groundwaters were used as a leaching solutions in unirradiated experiments. However, during the analyses (total inorganic carbon and organic carbon, speciation of organic carbon compounds) it was noticed that a high chloride concentration in the waters disturbed the sensitive analyses. Therefore, it was decided to replace the pH 12.5 solution with 0.01 M NaOH solution in the irradiated experiments.

2.2 Unirradiated materials

Loviisa steel and high carbon steel

The first unirradiated materials, which were used in preliminary leaching experiments, were Loviisa steel and Japanese high carbon steel. The carbon contents were 0.08 % and 1.2 %, respectively. Loviisa steel is Russian 08Z18H10T steel, which is Ti-stabilised austenitic stainless steel. It is identical with the steel components of the core of the Loviisa reactor. Japanese high carbon steel was the most pure carbon steel available. The chemical composition of Loviisa steel was analysed with optical emission spectrograph (OES) with combustion equipment (LECO) from a cross section. According to the analyses, the material composition was within the nominal composition of AISI321 (Table A1-2, App. 1). Subsequently, the cross section was etched to reveal the microstructure (SEM, Figure A1-1, App. 1). The SEM analysis showed that carbon existed mainly as interstitial atoms in the austenitic steel lattice. Cementite (Fe_3C) was not observed. Small white precipitates were observed in the etched structure of Figure A1-1 (App. 1). According to the EDS analysis, the precipitates were rich in Ti and C. The composition of Japanese high carbon steel, which is not stainless, is given in Table A1-2 (App. 1). The main form of carbon is carbide. These data are from the manufacturer. For the leaching experiments, the solid specimens were sawed to small fragments with a band saw and purified afterwards with acetone and isopropanol. Finally, the fragments were rinsed with deionised Milli-Q water.

Iron carbide (Fe_3C) and AISI316Ti steel powder

Because of the contamination difficulties in the grinding process of the preceding steel material, it was decided to prepare a new steel powder. The microstructure of Loviisa steel was shown to be comparable with the AISI321 steel (discussed above). The composition of the AISI316Ti steel is identical, but with a lower carbon content. Because of the better availability, AISI316 steel powder was acquired as a raw material for the preparation of the steel powder for the leaching experiments. The carbon content was increased to 0.3 % with gas atomisation method (VTT, Material modelling and eco design). Two batches with particle size of < 45 µm and 45 - 125 µm were prepared. Analyses were made to check the grain size and to confirm the presence of C as interstitial atoms with SEM/EDS and optical microscopy. The grain size was ~1 µm after gas atomisation. It differs from the grain size of Loviisa steel (~7 - 8 µm). Attempts were made to increase the grain size with heat treatment to correspond with Loviisa steel. Heat treatment caused some carbides to precipitate on grain boundaries. A decision was made to use the powder without heat treatment in the leaching experiments. The specific surface area for the batch with smaller particle size (< 45 µm) was determined based on the analysis of particle size distribution, which was measured with a particle size analyser (Mastersizer 3000 laser diffraction). The result was 509.4 m^2/kg.

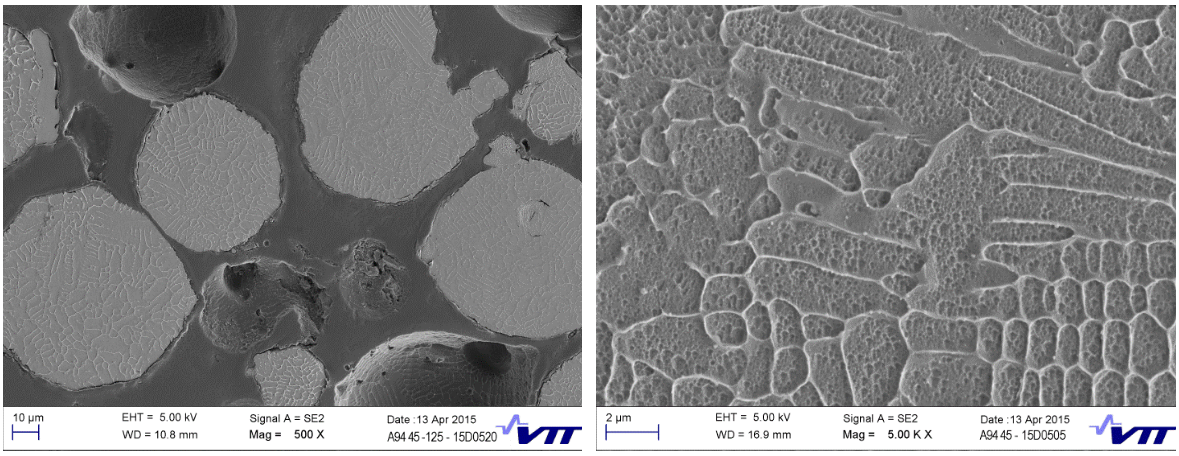

Figure 1: SEM pictures of AISI316Ti steel powder after gas atomisation.

A small batch of iron carbide powder (400 g) was received from a component manufacturer from USA, with the composition shown in Table 2. All carbon is as carbide (no free carbon). The specific surface area for the Fe_3C powder was analysed to be 17.60 m^2/kg.

Table 2: Composition of iron carbide powder.

Components	**Wt%**
Fe_3C	92.4
Fe	3.2
Fe_3O_4	3.4
SiO_2	0.58
Al_2O_3	0.31

2.2.1 Methods and experimental conditions

Preliminary leaching experiments (Loviisa steel and Japanese high carbon steel)
For the preliminary leaching tests two previously described materials, Loviisa steel and Japanese high carbon steel, were used. Materials were sawed to small fragments with a band saw and prior to the leaching experiments the fragments were washed with isopropanol and acetone.

The batch experiments were conducted in polypropylene vials in a glove box with Ar atmosphere (O_2<1 ppm, low CO_2). In addition to the Ar glove box, the test vials were kept in a closed steel container to ensure as homogenous gas phase as possible around the test vials between the samplings. The solid-liquid ratio (m/V) was varied as follows: 50 g/100 mL, 25 g/100 mL and 15 g/200 mL. The simulated groundwaters with pH 8.5 and 12.5 were used as leaching solutions.

Experiments with Iron carbide (Fe_3C) and AISI316Ti steel powder
As mentioned earlier, due to the uncertainties caused by possible contamination during the grinding process in the preliminary experiments, new materials for the leaching experiments were acquired and separated experiments for both gas and liquid phase samplings were started. The liquid phase experiments with Fe_3C powder as solid phase were started in April 2015 in DURAN® laboratory glass bottles (100, 150 and 250 mL) in the glove box with Ar atmosphere (O_2 < 1 ppm, low CO_2). The ratio of solid to liquid was varied as follows: 20g/80 mL, 50g/100 mL and 20g/200 mL. The experiments with modified AISI316Ti powder were started in June 2015. One ratio of solid to liquid (100g/200mL) was applied and three parallel tests were started. The gas phase experiments in anaerobic media bottles (100 mL) with septum stoppers were started in September 2015 and placed in the glove box.

2.3 Irradiated materials

The samples chosen for the irradiated experiments came from the surveillance capsule chains from the Loviisa nuclear reactor (Figure 2). These capsule chains were loaded in the Loviisa reactor (PWR) in the autumn 2011 and were removed in autumn 2015. The total irradiation time was 647.37 days. The capsules are used to determine the irradiation embrittlement of the pressure vessel during the operation of the reactor. The two specimens for ^{14}C leaching test were cut from these capsule chains. The composition of the unirradiated material (Table 3), which is stainless steel, was determined beforehand with optical emission spectrometer (Spectrolab S®). The nitrogen content of the unirradiated capsule steel was analysed to be 0.04 w-%. On the basis of this initial N content and the neutron dose fluence of the capsule, the theoretical maximum content of ^{14}C after exposure was calculated to be 2 x 10^3 Bq ^{14}C/g. according to the expression:

$$A = \lambda N,$$

where:

- N is the number of ^{14}C atoms created through the ^{14}N(n,p)^{14}C reaction per gram of sample materials; and
- $\lambda = \frac{\ln(2)}{T_{1/2}}$ is the radioactive decay constant of ^{14}C atoms, and $T_{1/2}$ = 5700 (Tuli 2005) y is the half-life of ^{14}C.

The computation of N follows from the time-integration of the ^{14}N(n,p)^{14}C reaction rate per atom (this reaction rate is denoted by n, and the transformation towards reaction rates per gram of sample material -N- is straightforward). The time domain is assumed to extend from t_0 to t_1, which corresponds to the irradiation history of the samples. Denoting by $RR(t)$ the time-dependent atomic reaction rate, we have that:

$$n = \int_{t_0}^{t_1} \int_{\forall E} \sigma_{n,p}(E)\phi(E,t)\, dE\, dt$$

The energy integral extends over the range of kinetic energy of neutrons, i.e., from 10^{-5} eV to 20 MeV. In practice, a multi-group formalism is adopted for the computation of the integral extended to the energy domain, thus reducing the integral to a sum of atomic reaction cross-sections, $\sigma_{n,p}^{g}$ and scalar neutron fluxes $\phi^{g}(t)$, where the energy variable E has now been dropped in favour of the group number g in the multi-group formalism.

The long half-life of ^{14}C allows us to neglect the radioactive decay elapsed during the irradiation cycles. In view of this, one can omit the calculation of multi-group scalar fluxes in favour of neutron *fluences*. The neutron fluence is defined as the time-integrated scalar flux:

$$\Phi(E) = \int_{\forall t} \phi(E,t)\, dt$$

In a multi-group scheme, group fluences Φ^{g} are used, which reduces the problem of activation to:

$$n = \sum_{\forall g} \sigma_{n,p}^{g}\ \Phi^{\mathrm{g}}$$

The computation of n involves two steps, namely

1. the determination of the multi-group activation cross sections $\sigma_{n,p}^{g}$ (a property of the material, independent of time); and
2. the calculation of the multi-group fluence Φ^{g} values, integrated over the irradiation history, and thus accounting for the location of the capsule, fluctuations in reactor power, as well as intra-cycle variations in the spatial and energetic distributions of neutrons within the reactor core.

The first step was conducted with the `NJOY` nuclear data processing system MacFarlane and Kahler (2013). Pointwise nuclear data was processed using a combination of Maxwellian, $1/E$, and fission spectra for the thermal, epithermal and fast ranges, respectively, at a temperature of 300 K. The cross section data was processed in the BUGLE-47 energy structure White (1996).

As for neutron fluences, their determination was the object of a careful calculation chain, where operational data from the core simulator was fed to the reactor dosimetry computer program `PREVIEW` Wasastjerna (1991). The output of this code is the neutron fluence at the surveillance positions, also in the BUGLE-47 structure. Prior to putting these fluence values to use, an additional spectrum adjustment step was carried with the `LSL-M2` code Stallman (1986) in order to procure multi-group fluences that maximize the agreement with experimental activity data for reactions spreading over a wide energy domain.

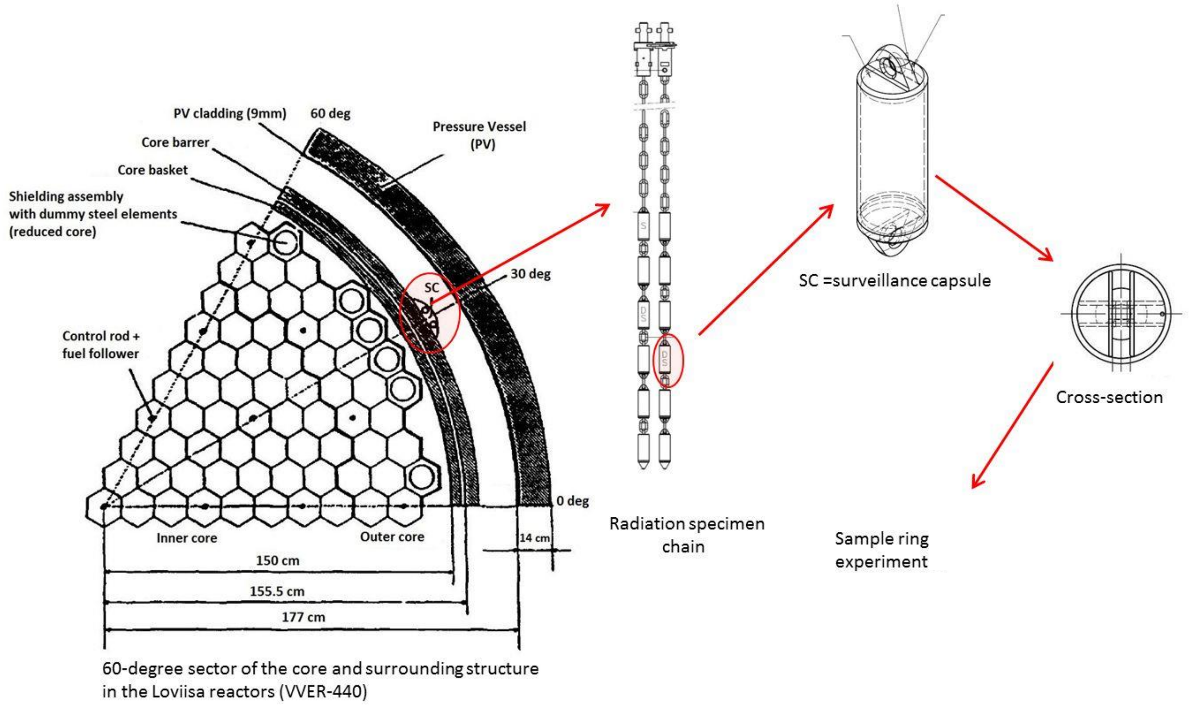

Figure 2: Schematic drawing of the surveillance capsule and its position in the reactor (Pictures by Fortum Power and Heat Oy).

Table 3: The composition of the inactivate surveillance capsule material.

Sample	**Composition (%)**							
Capsule cover	***C***	***Si***	***Mn***	***S***	***P***	***Cr***	***Ni***	***Mo***
	0.023	0.34	1.81	-	0.027	16.7	11.1	2.06
	Cu	***Al***	***W***	***V***	***Ti***	***Co***	***N***	***Fe***
	0.26	0.023	0.02	0.05	0.22	0.07	0.04	(rest)

Before starting the experiments activities of the specimens were determined with calibrated gamma spectrometer. Measured activities are presented in Table 4.

Table 4: Measured activities and weights of the two specimens selected to leaching experiment.

Specimen	**Total activity (MBq)**	**Weight (g)**
A	227.27	2.975
B	619.23	9.211

2.3.1 Methods and experimental conditions

The experimental set-up, which consisted of a zirconia crucible (Vol. 175 mL) placed inside of a 500 mL Duran glass bottle, was placed inside an under pressure glove box behind a lead shield (Figure 3) at room temperature and 1 atm. Prior the experiments were started the specimens were quickly rinsed with ethanol and weighed.

The experiments were started in June 2016 by immersing the irradiated specimens into the solutions. Specimen A (227.27 MBq) was immerged in pH 8.5 solution (CA85) and the more active specimen B was immersed in 0.01 M NaOH solution.

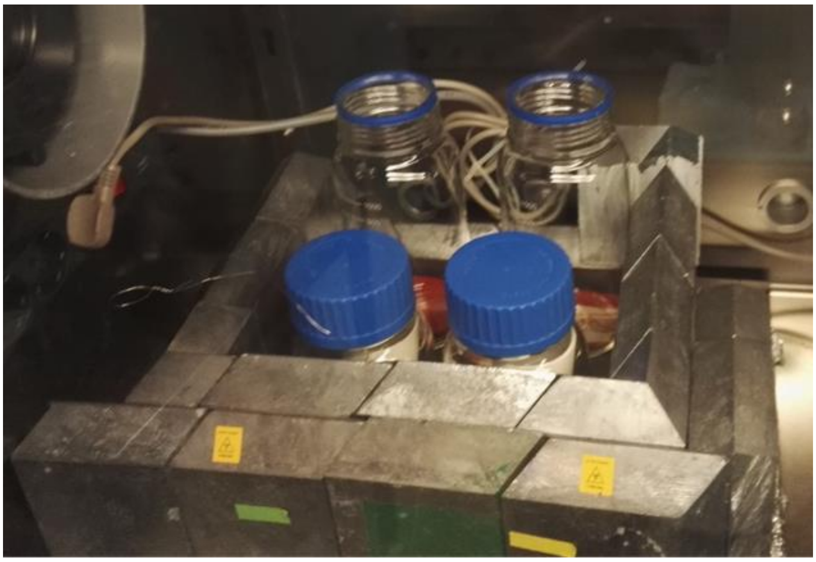

Figure 3: The experimental set-up inside of the glove-box behind the lead shield.

3 Results

3.1 *Experiments using unirradiated materials*

3.1.1 Preliminary leaching experiments

The pH values of the solutions were measured prior to the experiments and each sampling (Table 5). The redox potential of the solutions was measured 70 days after initialising the leaching tests (gold electrode, Ag/AgCl/ 3M KCl). The experiments with high carbon steel at pH 8.5 developed extremely reducing redox conditions with E_h value lower than -400 mV, which is close to the end of the stability field of water. The results of pH measurements showed that the higher pH 12.5 remained relatively stable during the experiments, but the lower pH 8.5increased close to the pH value 10.

Table 5: Experimental conditions of the preliminary leaching experiments.

Test code	**Solid material**	**m(g)/V(mL)**	**pH (initial)**	**pH (70 days)**	**pH (180 days)**	**E_h (70 days)**
LT-CA125(1)	Loviisa Steel	50/100	12.4	12.1	12.2	-223
LT-CA125(2)	Loviisa Steel	25/100	12.4	12.2	12.1	-209
LT-CA85(1)	Loviisa Steel	50/100	8.5	9.9	9.9	-231
LT-CA85(2)	Loviisa Steel	25/100	8.5	9.7	9.8	-228
YHT-CA85(1)	High carbon steel	50/100	8.5	9.9	9.7	-413
YHT-CA85(2)	High carbon steel	15/100	8.5	9.4	10.6	-483

Five samples were collected after subsequent leaching periods and the total amounts of dissolved inorganic carbon (DIC) and organic carbon (DOC) were analysed. The first sampling was done after the leaching time of 75 days. Due to the relatively high measured organic carbon content in the leaching solution, contamination during grinding was suggested and therefore the whole leaching solution was changed to a fresh simulant groundwater solution. Following samplings were done after total leaching times of 160, 256, 368 and 544 days. After each sampling only the sample volume of fresh leaching solution was added so that the m/V remained the same during the whole experiment.

TIC and TOC analyses were done for filtered samples (75 d: Whatman™, Puradisc FP30 syringe filters, 160, 256, 368 and 544 d: Sleicher & Schuell, Spartan 30/0.45 RC filters) with TOC analyser (Analytika Jena N/C UV HS) in Ramboll analytics. The analytical method is based on SFS-EN 1484 standard, in which organic carbon in solution is oxidised to carbon dioxide by hard UV radiation supported wet chemical oxidation. Carbon dioxide formed by oxidation is determined directly with non-dispersive infra-red (NDIR) detector. Before the TOC analysis, inorganic carbon is removed from the sample solution by acidification and purging and TIC can be determined separately. Due to the high salinity of the samples, dilution (1:2, 1:3) was necessary. Therefore, the measured contents for inorganic carbon were close to the limit of detection (0.1 mg C/L).

The results of the preliminary leaching tests are presented in Figure 4, Figure 5, Figure 6 and Figure 7. Figure 4 shows the results from two leaching tests (m/V, 50 g/100 mL and 25 g/100 mL) with Loviisa steel at pH 12.5. Dissolved inorganic and organic carbon contents were measured from filtered samples. The results show that the amount of dissolved organic carbon is higher in both samples. Relatively high organic carbon contents suggest contamination from the filter material (cellulose) or from the grinding process of the solid steel material. The purification after grinding may have not been successful to remove all oil and grease from the grinding process. The bigger mass of solid steel material in the same volume of leaching solution results in higher amount of dissolved carbon, which is expected.

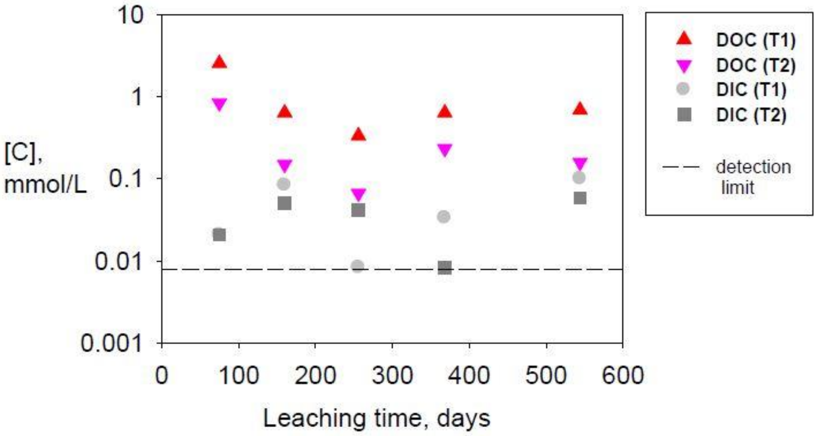

Figure 4: Dissolved inorganic (DIC) and organic (DOC) carbon in the preliminary leaching tests of Loviisa steel in simulated groundwater at pH 12.5 as a function of leaching time. T1 represents tests with m/V= 50 g/100 mL and T2 tests with m/V= 25 g/100 mL.

Figure 5 shows the concentration of dissolved organic ^{12}C in two leaching tests (m/V, 50 g/100 mL and 25 g/100 mL) with Loviisa steel at pH 8.5 and 12.5 as proportion to experiment time. The content of organic carbon increases slightly with pH. It seems that the concentration of carbon is decreased by time. This might be due to the addition of fresh leaching solution after each.

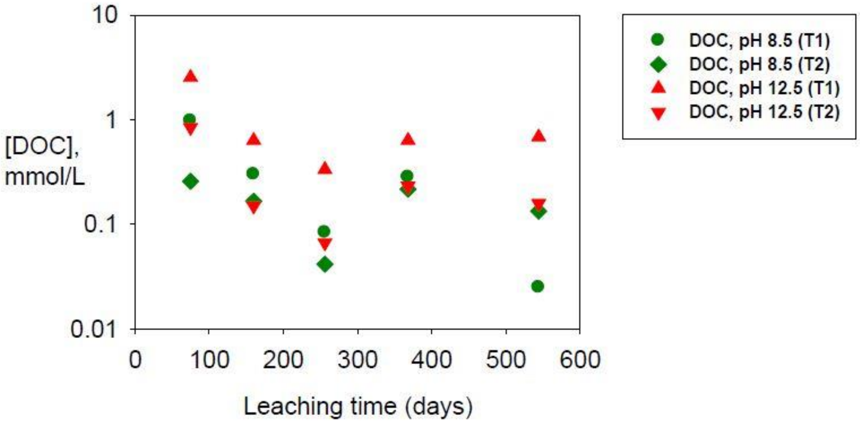

Figure 5: Dissolved organic carbon (DOC) in the preliminary leaching tests of Loviisa steel in simulated groundwater at pH 8.5 and 12.5 as a function of leaching time. T1 represents tests with m/V= 50 g/100 mL and T2 tests with m/V= 25 g/100 mL.

Figure 6 and Figure 7 show the measured DOC and DIC in leaching tests with both steel materials: Loviisa steel (Figure 6) and Japanese high carbon steel (Figure 7) at pH 8.5. The DOC is higher than the DIC in both tests. However, the content of inorganic carbon is higher in the tests with High carbon steel than that in the tests with Loviisa steel. The content of organic carbon decreases with increasing leaching time. The content of inorganic carbon increases slightly after 400 days of leaching.

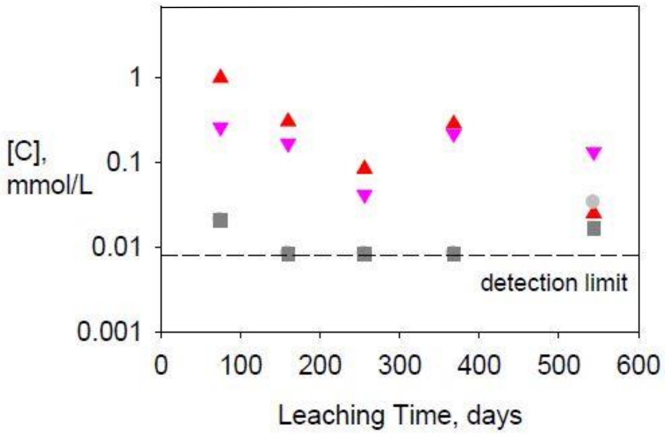

Figure 6: Dissolved organic (red and pink) and dissolved inorganic (grey) carbon in the preliminary leaching tests of Loviisa steel in groundwater at pH 8.5 as a function of leaching time.

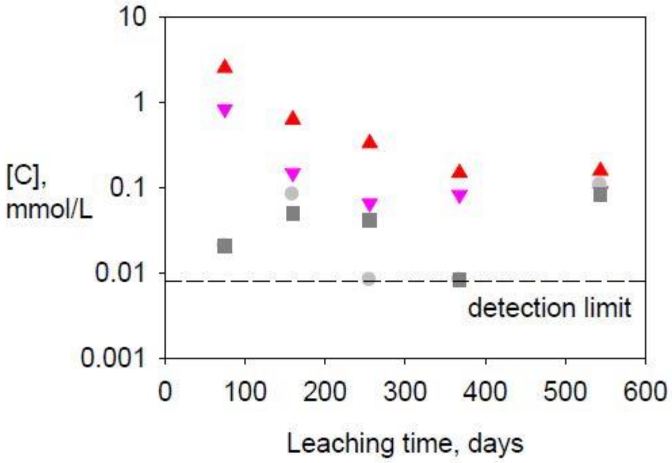

Figure 7: Dissolved organic (red and pink) and dissolved inorganic (grey) carbon in the preliminary leaching tests of High carbon steel in groundwater at pH 8.5 as a function of leaching time

3.1.2 Leaching experiments with Fe_3C and steel powders: Liquid phase

As in the preliminary tests the total amounts of dissolved organic carbon (DOC) and inorganic carbon (DIC) as well as the composition of organic carbon compounds in liquid phase were determined. The first samplings for the Fe_3C experiments were done after a leaching period of 20 days and for the modified AISI316Ti experiments after 48 days. The samples were prepared by first rinsing the filters (Whatman®) GD/X syringe filters, glass microfiber membrane, pore size 0.45 µm) twice with 10 mL Milli-Q water and then filtering 10 mL of leachate in 50 mL DURAN® glass bottle. Due to the high salinity of samples they were diluted to a total volume of 50 mL with Milli-Q water. In order to keep a constant m/V ratio in the experiments, 10 mL fresh leaching solution was added after the samplings. The results from the leaching test with Fe_3C and modified AISI316Ti powders at pH 8.5 and pH 12.5 are presented in Figure 8 (solid to liquid ratio ½). The distribution between inorganic and organic carbon from the experiments is calculated in Table 6. It seems that in all experiments the majority of the carbon was released in organic form. This is in good agreement with results of other WP2 partners. However, the proportion of inorganic carbon released in to the liquid phase, especially in higher pH experiments, was considerably higher in our experiments. This might originate from the atmospheric CO_2 during the analyses. These samples were always the last ones to measure, so they may have been contacted with air longer that others.

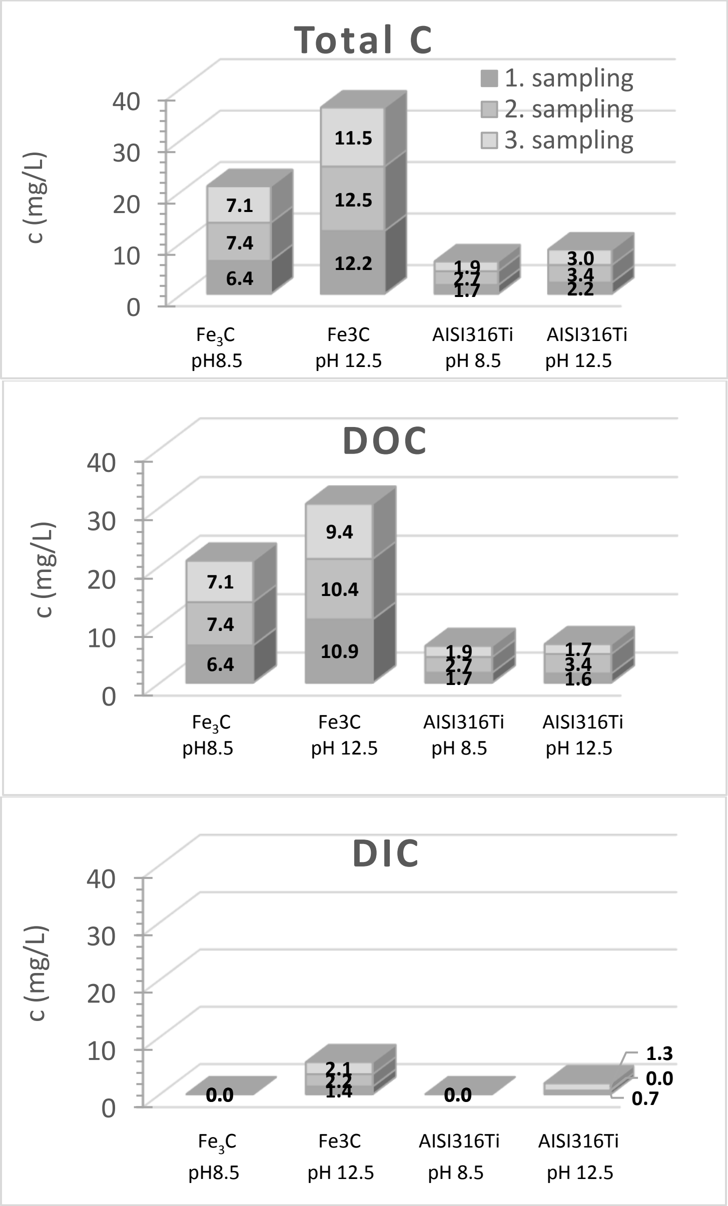

Figure 8: The total dissolved carbon content.

Table 6: Distribution of carbon in organic and inorganic form.

Material	**Leaching solution**	**C in organic form (%)**	**C in inorganic form (%)**
Fe$_3$C	*pH 8.5*	100	0
	pH 12.5	84	16
modif. AISI316Ti	*pH 8.5*	100	0
	pH 12.5	76	24

The carbon release rates from both materials were calculated and the results are presented in Table 7. More carbon seems to be released in higher pH experiments (pH 12.5). Although, AISI316Ti steel powder has much lower carbon content, relatively more carbon was released from AISI316Ti stainless steel powder compared to Fe_3C powder. The high inorganic carbon concentration determined from the solutions might also be contamination from the atmosphere.

Table 7: C release rates for Fe_3C and modified AISI316Ti stainless steel powders (fraction/yr).

Material	pH 8.5 solution	pH 12.5 solution
Fe_3C	1.7×10^{-4}	3.1×10^{-4}
modif. AISI316Ti	2.2×10^{-3}	3.1×10^{-3}

The composition of the organic carbon compounds in liquid phases were analysed at VTT Expert Services Oy and at VTT Oy. Volatile organic alcohols were analysed by gas chromatography with a flame ionisation detector (HS-GC-FID). The concentrations were detected by means of the external calibration with standards made of pure substances and the identifications were confirmed with standard additions. Other volatile organic compounds (VOCs) were analysed by HS-GC-MS instrument (headspace technique with gas chromatography and mass spectrometry). The compounds detected were identified by using commercial mass spectrum library and the concentrations were determined semi quantitatively with an external toluene standard. ESI-MS/(MS) and LC-MS/(MS) (electrospray ionisation tandem mass spectrometry, liquid chromatography tandem mass spectrometry) with a C18 column were used for the qualitative analysis of polar molecules sharing similar structures. The analyses were tested with undiluted and diluted samples. It was observed that quite high salt concentrations in the samples disturbed analyses and only adduct signal clusters coming from salt and LC-eluent (water-acetonitrile) were detected. Due to that the solid phase extraction (SPE) procedure was used to remove the salts and to concentrate the samples more. Both positive and negative ionisation modes were used in the measurements. For the compounds detected, the product ion spectra were measured. Possible organic acids, such as oxalic, formic, succinic, glycolic, acetic, lactic, levulinic, butyric and Valeric acids) were analysed by using a P/ACE MDQ capillary electrophoresis

(CE) instrument equipped with a photodiode array UV-Vis detector working indirect detection be wavelength of 230 nm (Beckman-Coulter Onc., Fullerton, USA). The acid standards were prepared and analysed prior to the analyses of the actual samples. The electrolyte solutions were commercial from Analis (Ceofix Anions 5 (Ordior/Analis, PART NUMBER: 10-0004680)). Bare fused silica capillary with inner diameter 75 µm, the detector length to the UV detector was 50 cm and the total length was 60 cm. The separation voltage of 30 kV and polarity of positive to negative were applied. Samples were injected using 0.5 psi pressure for 8 s. The separation of acids was carried out after diluting the sample by CE.

The volatile organic alcohols, which were analysed from the leaching solutions, were methanol, ethanol and 1-propanol. The results of the measurements are presented in Table 8: Results from the HS-GC-FID alcohol analyses. Only the concentration of 1-propanol in Fe_3C experiments was above the limit of quantification. On the other hand, the limit of quantification was relatively high, especially for methanol, with the method used (GC-FID) under these conditions.

Table 8: Results from the HS-GC-FID alcohol analyses.

Sample	Methanol (mg/L)	Ethanol (mg/L)	1-Propanol (mg/L)
Fe_3C *pH 8.5*	< 2	< 0.6	1.2
Fe_3C *pH 12.5*	< 2	< 0.6	2.7
modif. AISI316Ti *pH 8.5*	< 2	nd	< 0.3
modif. AISI316Ti *pH 12.5*	< 2	nd	< 0.3

< = detected, but concentration below limit of quantification (<LOQ)
nd = not detected

Other volatile organic compounds (VOCs), see Table 9, were determined with gas chromatography using MS detection in the samples from the leaching experiments with alkaline pH 12.5. Minor amounts of toluene, ethyl benzene and xylenes were found in the Fe_3C samples.

Table 9: Results from the HS-GC-MS analyses.

Sample	**Toluene**	**Ethyl benzene**	**Xylenes, sum**	***SUM***
Fe_3C, pH 12.5	0.04	0.01	0.02	*0.06*
modif. AISI316Ti, pH 12.5	nd	nd	nd	*nd*

nd = not detected

The LC-MS total ion chromatograms (Positive ionisation mode) of the samples after the solid phase extraction (SPE) procedure are presented in Figure 9. The compound peaks coming from the samples are filled with black colour. The ESI-MS-spectra taken from the three peaks detected in the sample from Fe_3C test (pH 12.5) are given in Figure 10.

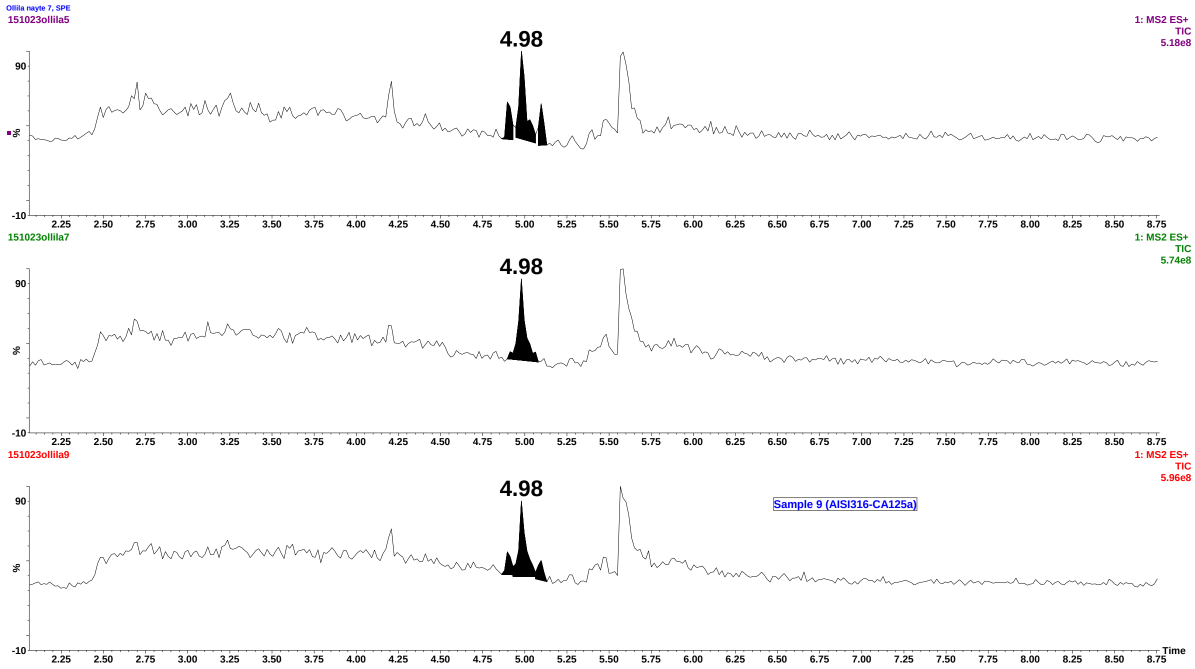

Figure 9: The LC-MS total ion chromatograms (positive ionisation mode) of the samples after SPE.

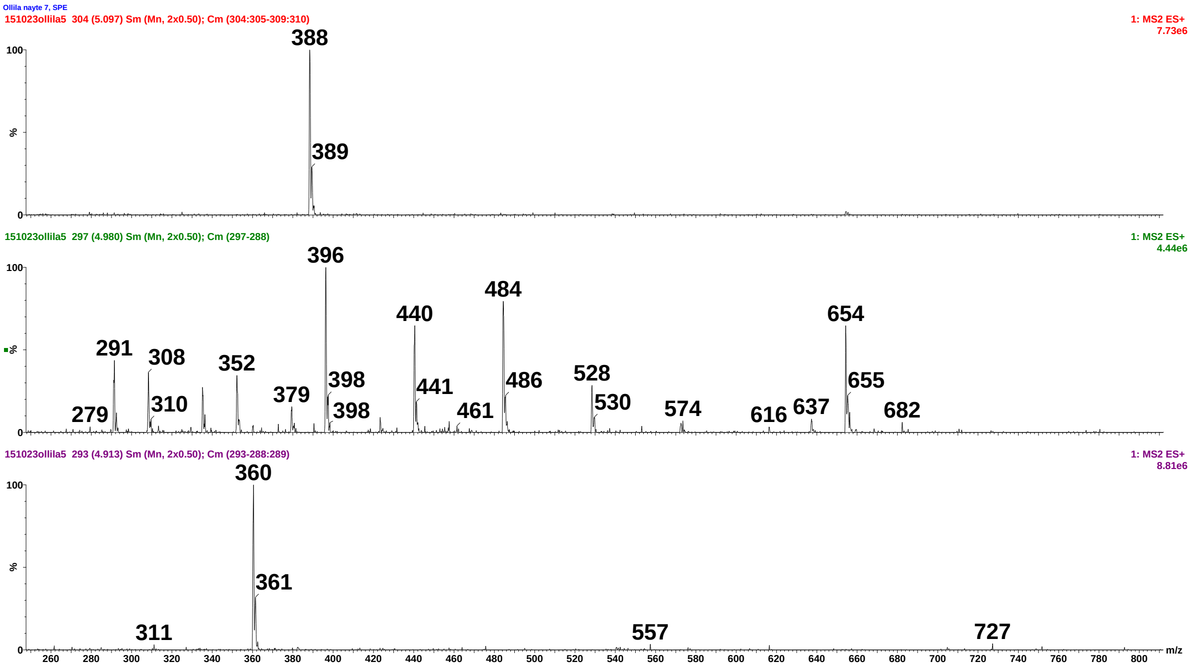

Figure 10: The ESI-MS-spectra taken from the three peaks detected in the sample from Fe$_3$C test (pH 12.5). Upper spectrum is a peak at the retention time of 4.91 min, middle at 7.98 min and bottom at 5.1 min.

Based on the product ion spectra and literature, the organic compounds detected in the sample from Fe$_3$C test (pH 12.5) were surfactants (tensides). The peaks at the retention times 4.91 (m/z 360) and 5.1 min (m/z 388) are probably hexadecyl (C16) and octadecyl (C18) benzyldimethelammonium chlorides. At the retention time of 4.98 min, the compounds detected were probably a mixture of alcohol ethoxylates (AE) or polyethylene glycols. The compounds with signal m/z 654 (Figure 10, middle spectrum) could not be identified but probably it is also a surfactant compound. These compounds were observed also in the samples from modified AISI316Ti test (pH 12.5). In the LC-MS/MS analyses with negative ionisation mode, also linear alkylbenzene silphonate (LAS) surfactants (tensides) were identified from both samples. Without reference standards the determination of exact concentrations could not be done. The rough estimation for the sum concentration of the surfactants was 1 -5 mg/L. In CE analysis no organic acids were detected. All the results were below the detection limit.

3.1.3 Leaching experiments with Fe_3C and steel powders: Gas phase

The gas phase analyses were performed in collaboration with the University of Helsinki. In qualitative analyses with m/z 10 -100 area, small hydrocarbons were identified in the gas phases of Fe_3C experiments at both pH 8.5 and 12.5 solutions. In gas phase samples taken from modified AISI316Ti stainless steel experiments no organic compound were detected. Compounds identified from the pH 8.5 experiments were ethane, propane, 2-methylpropane and pentane. From higher pH solution experiments (pH 12.5) we were able to identify following compounds: ethane, propane, propylene, butane, 2-buthene, 2-methylbutane, pentane, pentene and hexane. Additional gas phase analyses were performed later at VTT. Hydrocarbon compounds were analysed by gas chromatograph Agilent 6890N with Pulsed Discharge Helium Ionization Detector (PD-HID) with CP-Molsieve 5A column. The quantitative analyses gave similar results than the qualitative performed at the university. No organic compounds were detected in steel powder samples (AIAI316Ti). Instead, rather high methane and ethane concentrations were detected in the gas samples taken from Fe_3C experiments. The results are presented in the Table 10. Concentrations of CO and CO_2 in the gas phase were determined with Agilent 5890 gas chromatograph with flame ionization detector (FID) and Ni-catalyst methanor with GS-CarbonPlot column. Tentative results suggested around 1100-1900 ppm content of CO in the Fe_3C gas phase and minor concentration of CO_2 (10 ppm). In the course of the gas analyses, we observed clear overpressure inside the sample vessels.

Table 10: Results from the gas phase analyses.

	Fe_3C, pH 8.5	**Fe_3C, pH 12.5**	**AlSI316, pH 8.5**	**AISI316, pH 12.5**
	ppm	ppm	ppm	ppm
Methane (CH_4)	578	891	3	5
Ethane (C_2H_6)	245	428	0	0
Ethene (C_2H_4)	0	0	0	0
Propane (C_3H_8)	180	382	0	0
Propene (C_3H_6)	0	20	0	0
Asetylene (C_2H_2)	0	0	0	0
Iso-Butane (I-C_4H_{10})	21	46	0	0
Propadiene (C_3H_4)	0	0	0	0
N-Butane (N-C_4H_{10})	71	157	0	0
T-2-Butene (T-2-C_4H_8)	4	21	0	0
1-Butene (1-C_4H_8)	0	3	0	0
Iso-Butene (I-C_4H_8)	4	26	0	2
Cis-2-Butene (CIS-2-C_4H_8)	1	15	0	0
2-methylbutane (I-C_5H_{12}(	11	32	0	0
N-Pentane (N-C_5H_{12})	24	62	0	0
CO	*1190*	*1900*	*0*	*0*
CO_2	*10*	*10*	*10*	*10*

3.2 *Irradiated experiments*

The first samples from the irradiated experiments were taken after 133 days from the start. 1 mL and 4 mL samples from the liquid phase were taken to the gamma and beta measurements. Liquid scintillation counter (LSC) Wallac 1415, Protocol 81 was used to measure beta activity of the leaching solution. Gamma-emitting radionuclide activities in the solutions were determined with gamma spectrometry. Some precipitates (white in 0.01 M solution, yellowish in CA85 solution) were found in the solutions before the analyses (Figure 11).

Figure 11: Precipitation in the liquid samples taken from the experiment.

The activity measurements were performed without any pre-treatment of the solutions (e.g. ion exchange). Without the chemical separation it is impossible to identify present radionuclides, but it was suspected that they could be ^{55}Fe and ^{63}Ni or ^{14}C. In gamma measurements ^{54}Mn, ^{58}Co, ^{60}Co, ^{125}Sb ^{124}Sb and ^{110m}Ag nuclides were identified. Measured activities are presented in Table 11. Clearly higher activities were detected in CA85 solution experiment.

Table 11: Activities of the measured radionuclides in sample solutions.

Bq/g	**^{63}Ni/^{14}C ?**	**^{55}Fe**	**^{54}Mn**	**^{58}Co**	**^{60}Co**	**^{125}Sb**	**^{124}Sb**	**^{110m}Ag**
Specimen B in NaOH	4.6	11.1	0.4		1.2	2.0	0.7	0.4
Specimen A in CA85	131.9	1053.1	23.0	2.2	328.9	16.0	4.9	

4 Interpretation and conclusions

Site investigations and modelling studies suggest that the repository will eventually have reducing conditions. In the absence of oxygen the corrosion potential for steel in aqueous solutions is determined by the anodic (oxidation) and cathodic (reduction) reactions involved in the corrosion process. The estimated long-term general corrosion rate of stainless steel in anoxic alkaline conditions is <0.01 µm yr^{-1} but in the initial stage it could be higher than 10 µm yr^{-1} Smart et al. (2004). Long-term exposure of materials in a repository can result in significant alterations in materials during their service life Bairi et al (2010).

The experiments were started with unirradiated materials in order to test and improve the experimental procedures. The preliminary tests were stopped because of the possible contamination of the material during the sample preparation. Because the uncertainties concerning the form of carbon in irradiated steel structure two different materials were selected. In Fe(III) carbide (Fe_3C) powder carbon is in carbide form, whereas in modified AISI316Ti stainless steel powder carbon has been identified being as interstitial atom in the austenitic steel lattice. The results from the analyses from the liquid phase showed that the content of organic carbon was higher compared to inorganic carbon in all the experiments but especially in the experiments with Fe_3C. According to Vuorinen (2012), this is expected since the presence of carbides in metals seems to increase the formation of organic species at high pH. More carbon was released in higher pH experiments (pH 12.5) even though the corrosion rate should be lower at high pH and which was the case in the experiments with irradiated material AISI316Ti steel powder had much lower carbon content, but relatively more carbon was released from AISI316Ti stainless steel powder compared to Fe_3C powder. Hardy and Gillham (1996) have studied production hydrocarbons in aqueous solution systems. They detected hydrocarbons, including methane, ethane, ethane, propene, propane, 1-butene and *cis*-2-butene in the experiments. Possible sources for these organic compounds were considered to be: 1) carbon impurities in the metallic iron, 2) aqueous CO_2 and 3) other unidentified organic compounds dissolved in the source water. There is uncertainty concerning speciation of ^{14}C derived from neutron activation compared with bulk carbon in steels, which leads to uncertainty concerning also the speciation (e.g. CH_4, CO_2, CO, C_2H_2) of ^{14}C releases from irradiated materials compared with ^{14}C and ^{13}C. By selecting the two different powder types, carbon as carbide and interstitial atom form, we were trying to find if the initial form determines the form in which carbon releases into liquid and gas phase. Unfortunately, the concentrations of the organic species where so low and close to the detection limit that we were not able to answer this question. In order to improve the detection limit some pre-treatment of the solution phase (e.g. ion exchange, solid phase extraction) could be tested in order to lower the chloride concentration.The experiments with the irradiated surveillance capsule material were shorter than originally planned. Working inside a glove-box with such active material proved to be more challenging than expected. The results suggested stronger corrosion reactions at the lower pH of 8.5. This could be due to the higher chloride concentration in the simulated groundwater solutions but more probable reason was the lower pH. Corrosion of steel materials is increased in lower pH and higher chloride content Eurajoki (2010).

Due to the removal to the new laboratory facilities there has been a delay in the experiments. The experiments with irradiated steel were started in 2016 at our old building. The instruments, including the anaerobic glove-box, were then moved to the new building. However, we were not able to move the experiments to the new building since the licence to work with radioactive material was not in effect (and is not at the moment either) and we had to leave the specimens in the old building for storage without possibility to perform any sampling during this time. This delayed and prevented us from continuing according to initial plan. This work is also part in the Finnish national research programme (KYT2018) and is planned to be continued at least until 2018. The results will be published in at the end of KYT2018 program.

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Appendix 1

Table A1-1: The chemical composition of natural groundwater sample (LPVA5) collected from the nuclear power plant site Loviisa. pH of the water was 7.6 in the field and 7.5 afterwards in the laboratory.

Element/Species	**mg/L**
Ammonium, NH_4^-	0.89
Bicarbonate, HCO_3^-	104
Barium, Ba	0.037
Boron, B	0.31
Bromine, Br	18
Calcium, Ca	630
Chloride, Cl	5000
Cobolt, Co	0.002
Fluoride, F	1.1
Iodine, I	0.21
Iron, Fe (total)	1.8
Iron, Fe^{3+}	1.6
Lithium, Li	0.17
Magnesium, Mg	270
Manganese, Mn	3.1
Nickel, Ni	0.019
Potassium, K	25
Silicate, SiO_2	11
Sodium, Na	2200
Strontium, Sr	7.1
Sulphate, SO_4^{2-}	560
Total alkalinity, HCl uptake [mmol/L]	1.7
Total acidity, NaOH uptake [mmol/L]	0.18
Ionic strength [mol/kg]	0.21

Table A1-2: The chemical composition for Loviisa steel and Japanese high carbon steel.

Steel Material	**Loviisa steel (pipe 91452), Russian 08X18H10T steel**	**Japanese high carbon steel**
Structure	Ti-stabilised austenitic stainless steel, comparable with AISI321	Carbon steel with high purity available
Composition	*[%]*	*[%]*
C	0.08	1.2
Si	0.46	0.1-0.2
Mn	1.25	-
S	0.012	< 0.004
P	0.032	< 0.025
Cr	17.	
Ni	10.6	
Mo	0.13	
Cu	0.15	
Al	0.028	
W	0.04	
V	0.03	
Ti	0.521	
Co	0.07	
N	0.16	

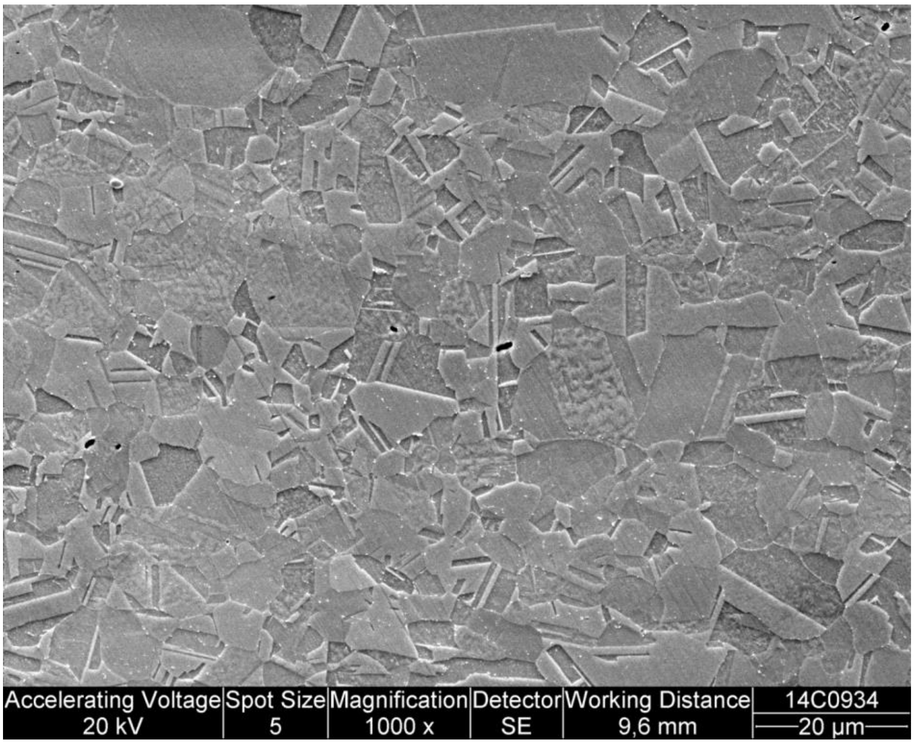

Figure A1-1: SEM picture of the surface of Loviisa steel.