DEMONI - Steel dissolution - Research notes 2020

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Summary

Carbon-14 is a typical activated product in metallic wastes and is mainly generated by the $^{14}N(n,p)^{14}C$ reaction. The corrosion phenomenon is considered to be a source of C-14 radionuclide into the groundwater. Carbon will be released from the metallic waste either as inorganic or organic form. The form defines the potential transport pathways that must be considered when assessing the migration of C-14 from the engineered system of a geological repository. The objective of this study is to investigate the release and speciation of C-14, especially the proportion of organic C-14 vs. inorganic C-14. The corrosion rate was expected to be very low under anaerobic conditions.

In KYT-DEMONI project new experiments with less active, pressure vessel material were started in 2019. This report presents the experimental setup of leaching experiments with irradiated stainless steel samples in simulant groundwater and groundwater from Loviisa. This report presents the first three samplings during 2020, separation of interfering nuclides with Chelex 100 resin, LSC measurement of C-14 with results and ICP-OES analysis of inactive elements with results as well. Experimental setup of started gas phase experiments is presented shortly as well.

Results of the first year's samplings from the solution phase experiments show very low corrosion rate about 0.00005 mm/a in Loviisa groundwater and about 0.00003 mm/a in groundwater simulant, which result in respectively about 0.02 % and 0.01 % release of the total C-14 inventory from the irradiated stainless steel piece. However, the measured activity concentrations in the solution phase sample are still low and close to the background and therefore uncertainties of the release rates and released fractions are high.

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Contents

1. Background and goal

Radioactive waste materials, such as activated stainless steel components, from nuclear power plants are expected to be disposed in an underground repository. Carbon-14 is a typical activated product in metallic wastes and is mainly generated by the $^{14}N(n,p)^{14}C$ reaction. The corrosion phenomenon is considered to be a source of C-14 radionuclide into the groundwater. Because of its long half-life of 5,730 years and special chemistry, C-14 is considered as an important radionuclide in safety assessment. Carbon can be released from the metallic waste either as inorganic or organic form. This defines the potential transport pathways that must be considered when assessing the migration of C-14 from the engineered system of a geological repository.

The European Commission CAST project (CArbon-14 Source Term), which ran from 2013 to 2018, aimed to develop understanding of the potential release mechanisms of C-14 from radioactive waste materials in geological disposal conditions. VTT was involved in the Work package (WP2), which was dedicated to steel materials. In CAST project the work was started with inactivated iron carbide and modified AISI316Ti steel powders to develop the experimental methods and protocols. The activated material used was the surveillance capsule chain from Loviisa nuclear reactor. Because of the high activity of the surveillance capsule material, the handling of the activated specimens turned out to be challenging in the anaerobic glove box behind the lead shielding. In KYT-DEMONI project new experiments with less active, pressure vessel material were started. The sampling of the remaining samples of activated steel from CAST project were included in the KYT-DEMONI project as well and the total C-14 analyses with LSC were finished during the beginning 2020. Later in 2021, CAST samples may be used for method development work, for analysis of organic and inorganic fractions in the solution samples.

The objective of this study is to investigate the release and speciation of C-14, especially the proportion of organic C-14 vs. inorganic C-14. The corrosion rate is expected to be very low under anaerobic conditions.

2. Leaching experiments

2.1 Experimental setup

First four experiments with irradiated steel samples were started in anaerobic glovebox in September 2019 [1]. Two experiments were started in simulant water and other two in groundwater from Loviisa. pH of each leaching solution was measured before starting the experiments. Prior putting into the leaching solution, stainless steel pieces were rinsed with ethanol. Table 1 shows detailed information of selected steel samples and Table 2 shows the composition of synthetic groundwater. In Table 3 is presented the experimental setup with added leaching solution details. It should be noticed that lower pH value in synthetic water might rise since the water was not in equilibrium with glove box atmosphere at the time pH was measured. During the personnel changes within VTT it was noticed that the chemical composition of prepared simulant water was different than originally was planned. Since similar activated steel samples are used in dissolution experiments in KYT DEMONI project in University of Helsinki and in the KYT TERKOR project in VTT and the aim is that results may be compared later. Therefore, new simulant water with correct chemical composition was prepared and two new solution phase experiments were started in December 2020. Tables 1, 2 and 3 include also the details of the two new experiments.

Table 1. Irradiated stainless steel pieces selected for leaching experiments.

Steel sample	Dimensions [cm] thickness x width x height	Volume [cm^3]	Mass [g]	Calculated density [g/cm^3]
TH_1	0.026 x 1 x 1	0.026	0.1407	5.412
TH_2	0.026 x 1 x 1	0.026	0.1426	5.485
TH_3	0.026 x 1 x 1	0.026	0.1427	5.488
TH_4	0.026 x 1 x 1	0.026	0.1439	5.535
TH_5[1]	0.026 x 1 x 1	0.026	0.1425	5.481
TH_12[1]	0.026 x 1 x 1	0.026	0.1433	5.512

[1] New solution phase experiment started in 7.12.2020; new simulant water with correct chemical composition.

Table 2. The composition of synthetic groundwater simulant leaching solutions. Solution was prepared and stored in the anaerobic glove box. Simulant water was prepared from milliQ water (Millipore).

Composition of the OLD simulant groundwater			
Added chemical	Added mass [g] / 2L of milliQ water	Anion	Amount in the final solution [mg/L]
NaCl	11	Cl$^-$	3336
Na$_2$SO$_4$	1	SO$_4^{2-}$	338
Composition of the NEW simulant groundwater			
NaCl	18	Cl$^-$	5500
Na$_2$SO$_4$	1.5	SO$_4^{2-}$	500

Table 3. C-14 leaching experiment setup and starting date of the experiments.

Experiment	Experiment started	Steel sample	Leaching solution	Added volume [mL]	pH prior experiment
S1	17.9.2019	TH_1	OLD Synthetic groundwater	500	5.99[2]
S2	17.9.2019	TH_2	OLD Synthetic groundwater	500	5.99[2]
L1	17.9.2019	TH_3	Loviisa groundwater	500	7.61
L2	17.9.2019	TH_4	Loviisa groundwater	500	7.61
SU1	7.12.2020	TH_5	NEW Synthetic groundwater	500	6.88[3]
SU2	7.12.2020	TH_12	NEW Synthetic groundwater	500	6.88[3]

[2] Simulant groundwater not in equilibrium with anoxic glove box atmosphere while pH was measured.
[3] Simulant groundwater in equilibrium with anoxic glove box atmosphere while pH was measured.

2.2 Sampling of the solution phase experiments

The first three samplings of the experiments S1, S2, L1 and L2 were done during 2020. About 40 mL of leaching solution was taken with needle and syringe through the rubber septum cap of each experiment bottle. Fresh leaching solution was not added so that solution would not be diluted which may have happened in the earlier experiments in the CAST project [2]. pH of each leaching solution was measured after sampling. Figure 1 shows the pH measurement results of each sample as a function of time passed since the beginning of the experiment.
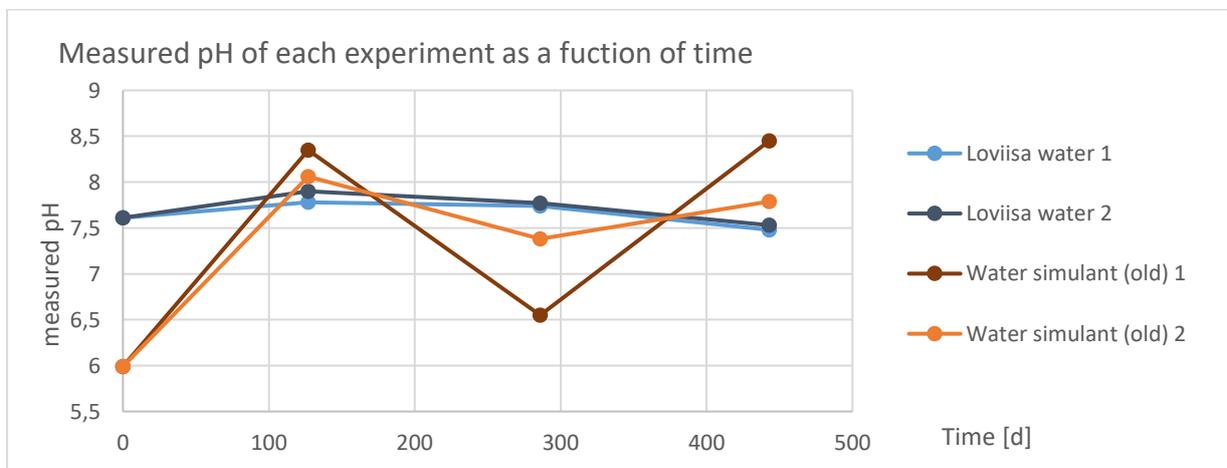
Figure 1. pH measurement results of each sample L1, L2, S1 and S2 as a function of time passed since the beginning of the experiment.

pH of Loviisa groundwater has stayed quite stabile within 0.5 pH units. As mentioned earlier the old simulant water was not in equilibrium with anaerobic atmosphere during the first pH measurement and it was assumed that the pH would rise while the equilibrium is reached, and this is the case. Within the three first sampling, pH of the old groundwater simulants is closer to values between pH 7- 8. However, the pH range is larger than in Loviisa groundwater experiments.

After sampling, the solution samples were transferred out from the anaerobic glove box and interfering radionuclides (Co-60, Fe-55 and Ni-63) were separated with Chelex 100 (Analytical grade) chelating ion exchange resin in sodium form [3]. Chelex 100 resin can be used for separation of polyvalent metal ions, since it has paired imonodiacetate ions, which chelate polyvalent metal ions. However, the resin does not interact with organic anion species. Chelex 100 resin is also stable in the alkaline solutions and resistant to radiation. [3]

Separation of interfering radionuclides was conducted in bach separations, where known amounts of Chelex 100 resin (1.5 g) and sample solution (25 mL) was added to a 50 mL centrifuge tube and tubes were shaken slowly for 24 h.

After separation, samples were centrifuged (3000 RPM, for 10 min) and 5 mL of supernatant was taken for liquid scintillation counting (LSC). Due to rather incoherent result from the first LSC, filtration of the samples was added as an additional sample preparation step after the centrifugation. Since the Chelex 100 resin is quite light and it will easily move after centrifugation, it is possible that small resin particles including some interfering radionuclides may be pipetted to the LSC sample and this may interfere with the measurement. Filtration the samples with 0.22 μm filter removes the possible interfering particles. Filtrated and unfiltered samples were measured, and results are presented and discussed in the next section. Some of the samples were also diluted (1/100 and 1/10) and stable elements in the sample solution were measured with ICP-OES equipment (5100 SVDV, Agilent Technologies). These results are also presented and discussed in the next section.

2.3   Analysis of sample solutions

2.3.1   ICP-OES analysis

Some of the samples were also measured with ICP-OES equipment (5100 SVDV, Agilent Technologies). Samples were diluted 1/100 and 1/10 with ultrapure 1 % HNO_3 solution. Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, S, Sb, Si, Sn, Ti, V, W, Zn and Zr were measured from the diluted samples. Multi-elemental standard solutions provided by Inorganic Ventures and SPEX were used as standards and control samples in the ICP-OES measurement.

2.3.2   LSC measurement of leaching experiment samples

First samples were measured for 30 min each with Hidex 300 SL liquid scintillation counter, however later the measuring time was increased to 2 h per samples. Samples which were not separated with Chelex 100 resin and samples separated with Chelex 100 resin were measured with LSC. In addition, samples separated with Chelex 100 resin and filtrated were measured after the 2nd and 3rd sampling, in order to see if the filtration actually has an effect on the measured activity concentrations.

2.3.2.1.1   Test for mixing ratio and chemiluminescence

Suitable sample solution and scintillation cocktail (Optiphase, HiSafe 3) was tested prior to the mixing of actual samples from the experiments. It can be assumed that at the beginning of the leaching experiment, the concentration of C-14 in the leaching solution is very low. Therefore, 5 mL and 10 ml of prepared simulant groundwater and groundwater from Loviisa was mixed with 10 mL of scintillation cocktail. In addition, control sample with similar ratios from milliQ water was prepared. After mixing, test samples were let to stand in dark for overnight prior the measurement, in order to minimise the effect of chemiluminescence. The test samples with ratio 10:10 mL stayed turbid and therefore 5:10 mL ratio was selected for the actual samples from the leaching experiments. Test samples were measured again next day in order to confirm the absence of chemiluminescence and the measurement results were equal to the first results. The sample-cocktail ratio 5:10 mL was used with all samples and in order to exclude chemiluminesence 12 h delay was used prior each LSC measurement.
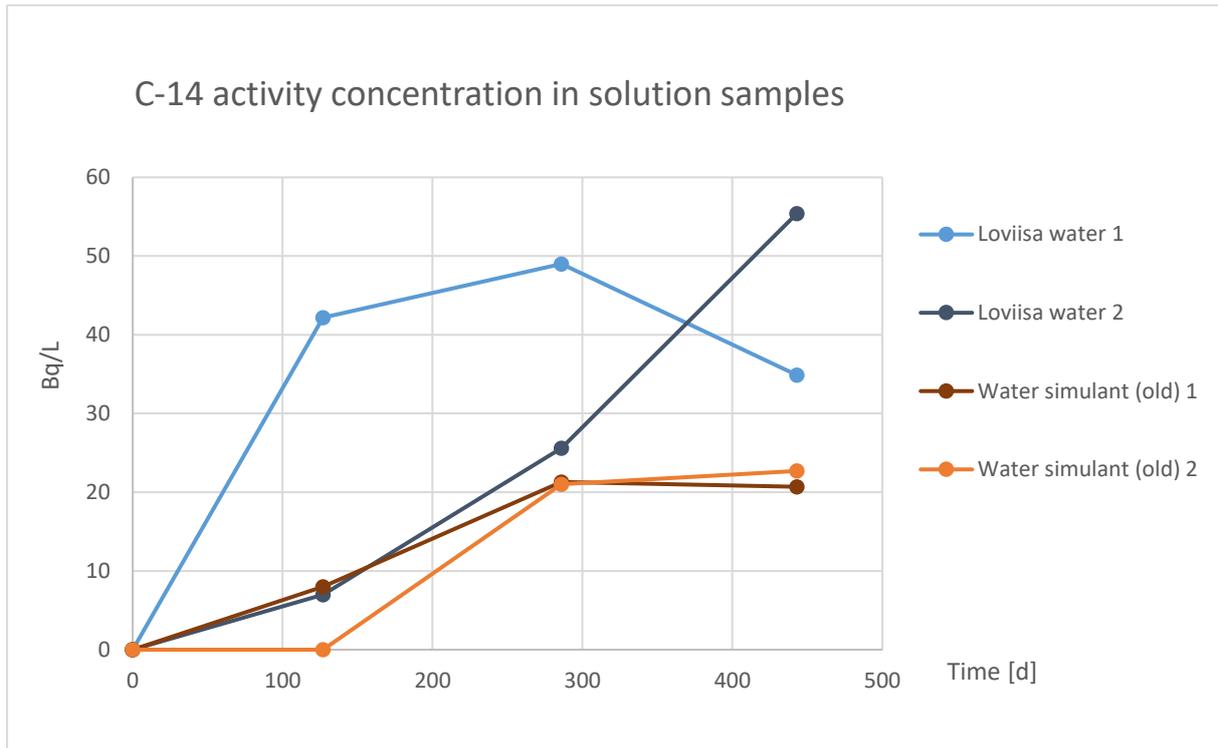
2.4   Results and discussion

2.4.1   Chelex 100 separation

Both separated and not separated samples were measured with LSC. Figures 2a and b show the measured activity concentrations in not separated and separated sample solutions.
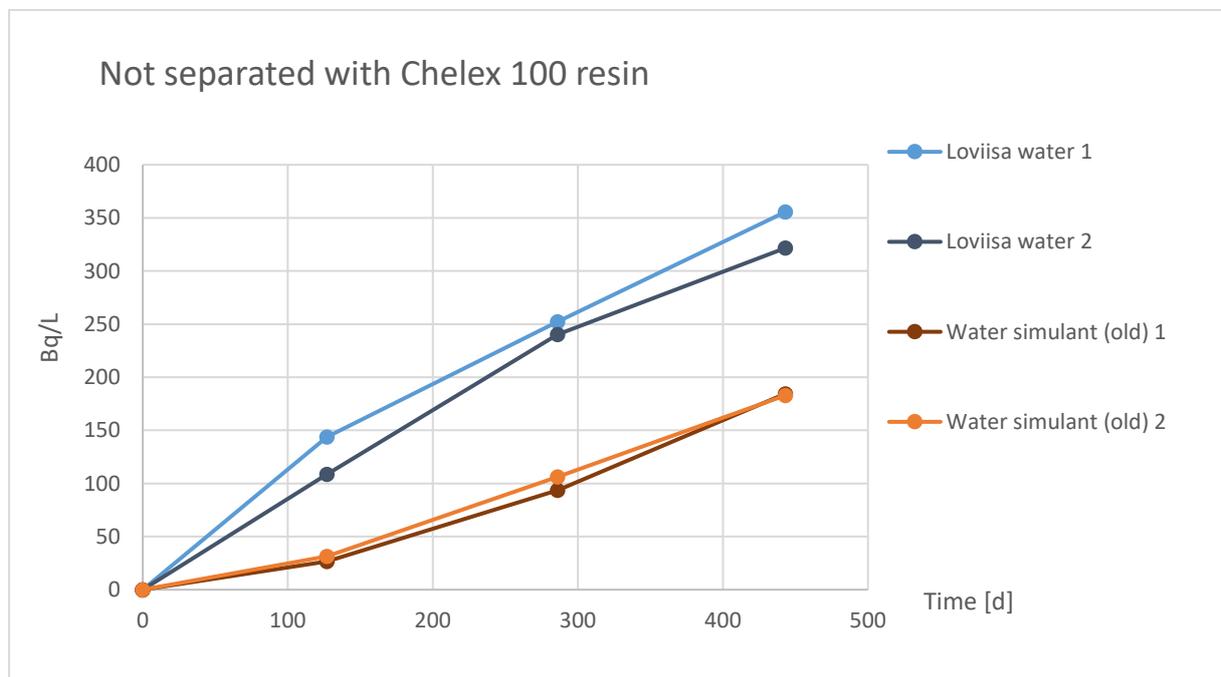
Figure 2a. *Measured activity concentrations in not separated sample solutions as a fuction of time.*

Figure 2b. *Measured C-14 activity concentrations in Chelex 100 resin separated sample solutions as a fiction of time.*

The measured activity concentrations of unseparated solutions are significantly higher than the activity concentrations measured from the separated ones. Therefore, it can be said that Chelex 100 separation removes significant part of interfering radonuclides from the sample solutions.

In order to evaluate the effect of Chelex 100 separation on the interfering radionuclides, stable elements were measured with ICP-OES equipment from the sample solutions. Especially stable elements Fe, Ni and Co were of interest, since their beta and gamma emissions may interfere the measurement of C-14 in LSC measurement. Ni-63 is pure beta emitter and Fe-55 decays through electron capture, so they cannot be identified in the LSC spectrum if they are mixed with C-14. Co-60 has high energetic gamma emissions and it is rather easy to measure with gamma spectrometry. However, since ICP-OES measurement were done anyways and its capability to give more information about the sample solutions, ICP-OES technique was used instead of gamma spectrometry. Also, the expected corrosion rate is low, so therefore measuring very low activities of Co-60 may be tricky, since measuring conditions and background should be kept very low and stable. Table 4 shows measured Fe concentration in the sample solutions. Unfortunately, the concentrations of Ni and Co in the solution were so low, that all measured results were under the limit of detection (LOD): < 0.013 mg/L for Ni and < 0.014 mg/L for Co.

Table 4. Measured concentrations of Fe in the sample solutions before and after the Chelex 100 resin separation.

Experiment and sampling date	day of the experiment	Before Chelex 100 separation [mg/L]	After Chelex 100 separation [mg/L]
S1 17.9.2019	0	< 0.004	0.01
S1 22.1.2020	127	0.01	0.02
S1 29.6.2020	286	0.38	< 0.004
S1 3.12.2020	443	0.42	0.01
S2 17.9.2019	0	< 0.004	0.01
S2 22.1.2020	127	0.04	0.01
S2 29.6.2020	286	0.89	0.01
S2 3.12.2020	443	1.82	0.02
L1 17.9.2019	0	0.09	< 0.004
L1 22.1.2020	127	3.44	0.01
L1 29.6.2020	286	2.21	0.01
L1 3.12.2020	443	2.71	0.01
L2 17.9.2019	0	0.09	< 0.004
L2 22.1.2020	127	0.12	< 0.004
L2 29.6.2020	286	1.11	< 0.004
L2 3.12.2020	443	1.45	< 0.004

Based on the measured Fe concentrations in the sample solutions, it can be said that at least Fe is removed during the Chelex 100 separation. ICP-OES measurements alongside with the LSC measurements should still be continued, in order to get a similar evidence for Ni and Co as well. This time samples were measured from the 1/10 dilution, so smaller dilution factor should be considered for the next measurement if the total dissolved solids (TDS%) is low enough for lower dilution factor.

2.4.2 Effect of filtration

Figure 3 shows the measured C-14 activity concentrations in the unfiltered and filtered (0.22 µm filter) sample solutions from the 2nd and 3rd samplings.
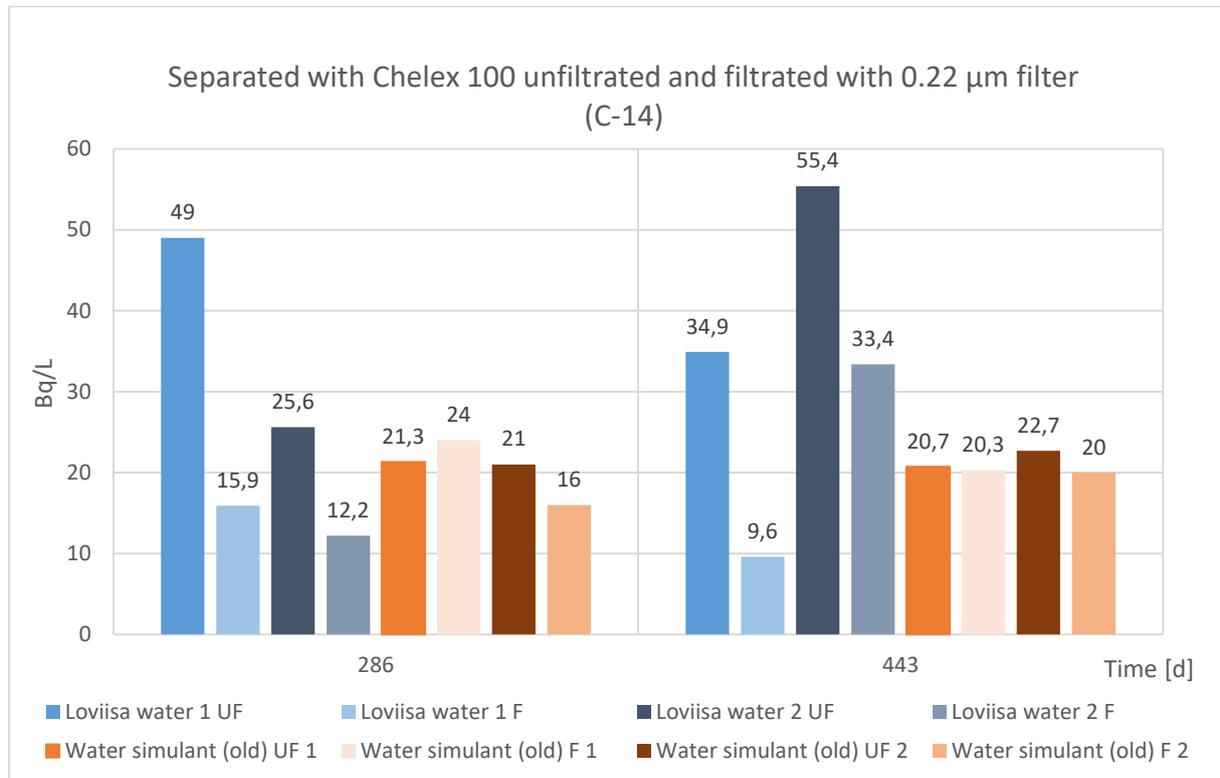

Figure 3. *C-14 activity concentration in unfiltered and filtered sample solutions from the 2nd and 3rd sampling in 2020. UF refers to unfiltered and F refers to filtered samples.*

Filtration seems so have bigger impact on the activity concentration on the Loviisa water samples that for the simulant water samples. This could mean that C-14 is attached to some larger compound that can be removed by filtering. For the groundwater simulants there is not significant difference between the filtered and unfiltered results. Also as previously mentioned, Chelex 100 separation is effective at least in the case of Fe. Therefore, only the unfiltered results are used from now on, and filtering is not required during each sampling. After the installation, commissioning and method development of Ion chromatography (IC) equipment to VTT's CNS laboratory, filtered and unfiltered samples may be analysed with IC and some additional info could be find out.

2.4.3 Groundwater stability and composition

As presented previously the pH of the simulant groundwater and Loviisa water has stayed rather stable during the leaching experiments. ICP-OES measurement results showed that the macro elements in the sample solutions have stayed stable as well. Figure 4 and 5 show the measured concentrations of S and Na in the sample solutions. Original target values for Na and S are also informed in the pictures.
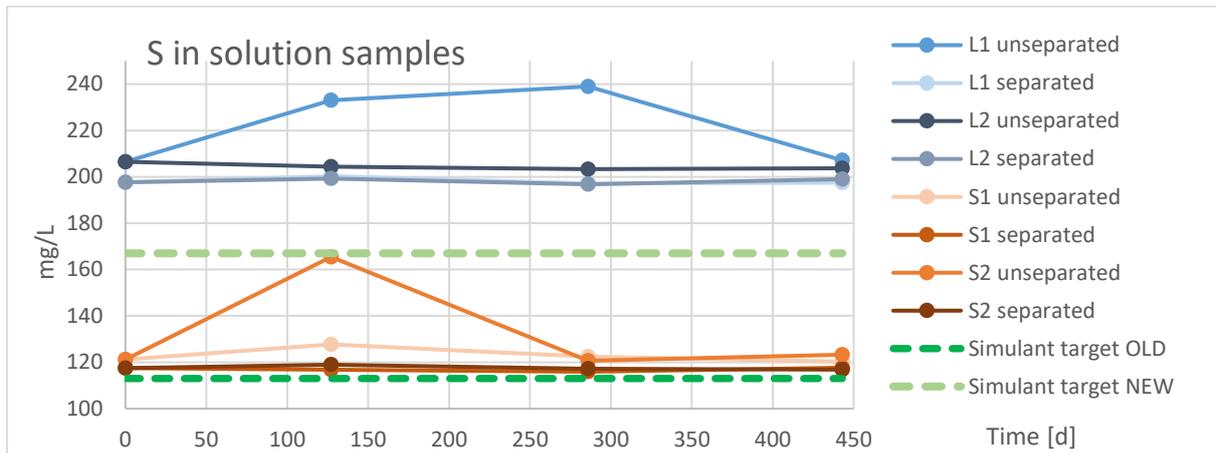
Figure 4. *S concentration in the measured sample solutions and target values for S concentration in the OLD and NEW groundwater simulant. Unseparated refers to samples without Chelex 100 resin separation and separated refers to samples with Chelex 100 separation.*

Simulant groundwater S concnetrations are close to target value for the OLD groundwater simulant. Loviisa groundwater S results are significantly higher than those in the simulant groundwaters. Therefore, it was reasonable to start the two new leaching experiments with NEW groundwater simulant that has S concentration closer to Loviisa groundwater values.
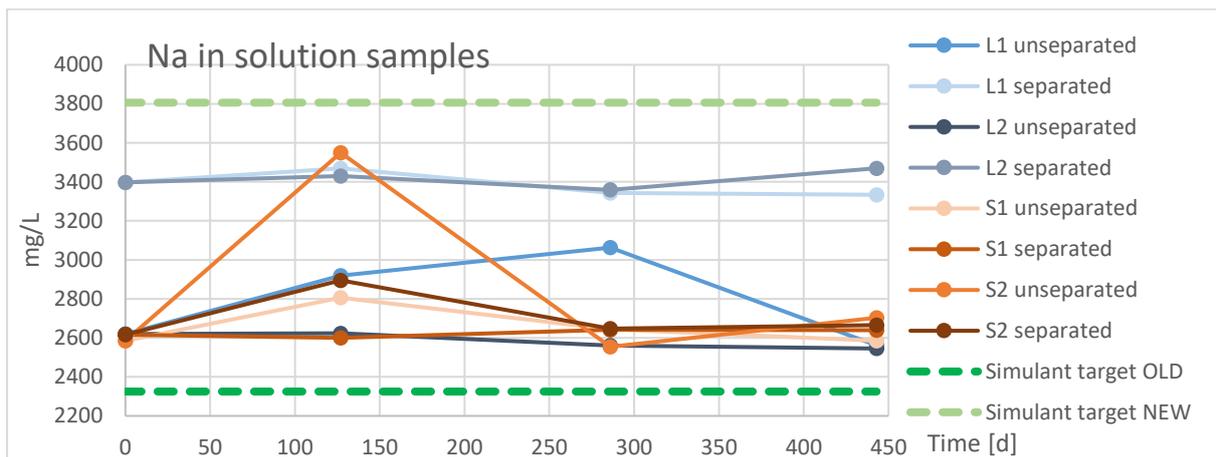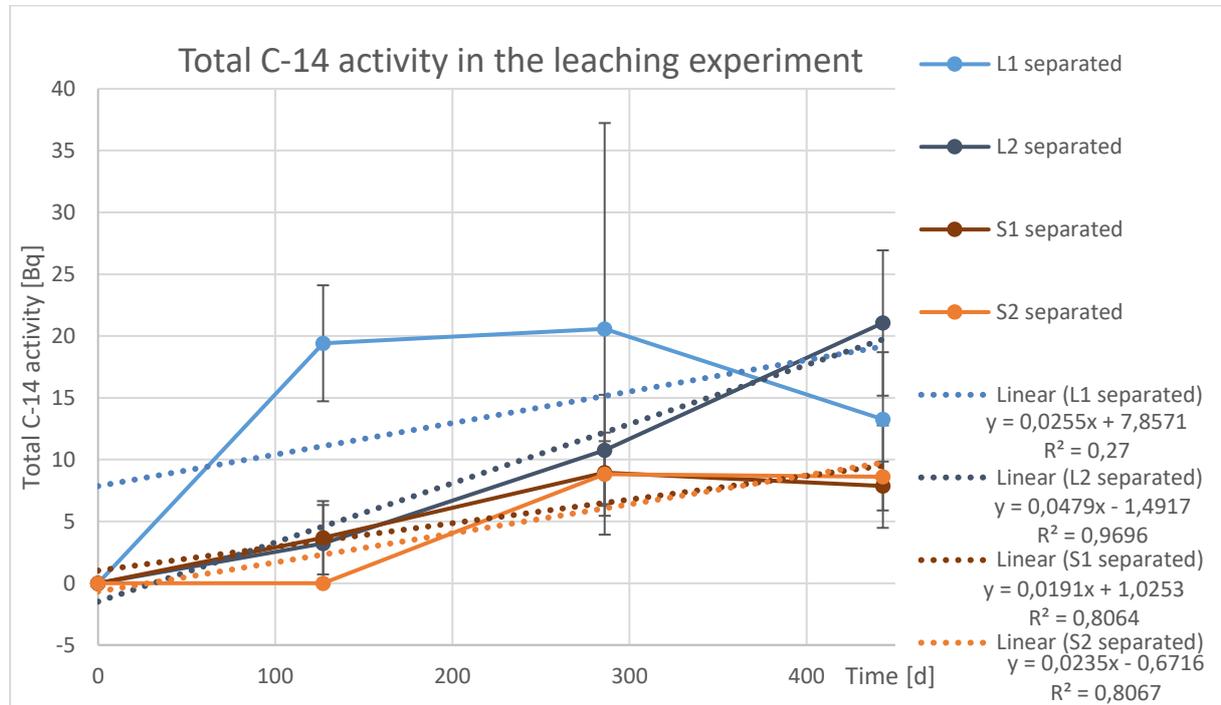

Figure 5. *Na concentration in the measured sample solutions and target values for Na concentration in the OLD and NEW groundwater simulant. Unseparated refers to samples without Chelex 100 resin separation and separated refers to samples with Chelex 100 separation.*

Na concentrations in the solution samples have more fluctuation. Actual measured values are between the OLD and NEW simulant water target values.

2.4.4   C-14 release and corrosion rate

Figure 6 shows the total C-14 activity in the whole leaching solution and 95 % confidence level uncertainty for C-14 activity as a function of time.

Figure 6. *Total C-14 activity in the whole leaching solutions. Uncertainty is 2 x Standard deviation of the measurement.*

Since the measured activity concentrations are still low and close to the background of LSC measurement, uncertainties are high. Two parallel Loviisa groundwater results have quite a bit of fluctuation. However, based on the trendline equations the C-14 release after 1 year (365 d) of the leaching experiments can be calculated. Table 5 shows the calculated C-14 fractions released during the first year of the leaching experiment with uncertainties. Table 5 present also released percentage fraction of the whole C-14 inventory based on the NKS-429 publication [1] and corrosion rate, assuming that C-14 is homogenously distributed in the stainless steel piece.

Table 5. Total C-14 release during the first year of the leaching experiments.

Experiment	Total C-14 release during the first year [Bq/a]	Original C-14 activity of the stainless steel piece based on [1] and sample masses [kBq]	C-14 released fraction [%]	Corrosion rate [nm/a]
L1	17.16 ± 41.0	76.12 ± 43.6	0.023 ± 0.055	55 ± 14
L2	15.99 ± 3.0	77.15 ± 44.2	0.021 ± 0.013	51 ± 3.1
S1	8.00 ± 6.2	77.20 ± 44.2	0.011 ± 0.010	26 ± 2.5
S2	7.91 ± 5.7	77.85 ± 44.6	0.010 ± 0.010	25 ± 2.4

As mentioned before, the uncertainties are still high due to the low C-14 activity concentrations in the solution samples. Therefore, the fitting of the trendlines is not ideal, especially with sample L1. Hence, more leaching time is required in order to get higher activity concentrations into the solution to be measured with LSC and further improve the reliability of the results. It is also interesting to see how the change in the groundwater simulant composition will influence the release of C-14.

3. Gas phase experiments

Six new gas phase experiments were started in 14th of December 2020. Three experiments were started in NEW simulant groundwater and other three in groundwater from Loviisa. pH of both leaching solution was measured before starting the experiments. Stainless steel pieces were weighted, rinsed with ethanol (AA) and dried in Ar glove box atmosphere prior starting the experiments. Table 6 presents the details of irradiated stainless steel pieces used in the gas phase experiments.

Table 6. Irradiated stainless steel pieces selected for gas phase experiments.

Steel sample	Experiment	Dimensions [cm] thickness x width x height	Volume [cm^3]	Mass [g]	Calculated density [g/cm^3]
TH_6	L1G	0.026 x 1 x 1	0.026	0.1449	5.573
TH_7	L2G	0.026 x 1 x 1	0.026	0.1398	5.377
TH_11	L3G	0.026 x 1 x 1	0.026	0.1430	5.500
TH_9	S1G	0.026 x 1 x 1	0.026	0.1419	5.458
TH_8	S2G	0.026 x 1 x 1	0.026	0.1408	5.573
TH_10	S3G	0.026 x 1 x 1	0.026	0.1505	5.789

Since C-14 activity concentrations have been quite low in the solution phase experiments, the liquid volume of gas phase experiments was decided to be smaller. 80 mL of Loviisa groundwater or simulant groundwater was added to each experiment. With this amount, sufficient gas volume was left in the experiment bottle for gas phase sampling and further analysis. Sampling of the gas phase experiments will be started in 2021 and analytical method for analysing C-14 in the gas phase will also be studied during 2021.

4. Plan for future work

In 2021, the work will continue with the dissolution experiments started at VTT in 2019 with irradiated pressure vessel material in contact with Loviisa groundwater and OLD and NEW versions of groundwater simulants. The sampling is planned to be carried out 2 times a year. Sampling of the experiments with NEW groundwater simulant will be started in 2021 as well. After the sampling Chelex 100 resin separations and analysis with LSC will be continued. ICP-OES measurement of the sample solutions will be done alongside with the LSC measurement and the lower dilution factors for ICP-OES measurement will be considered. After the installation and commissioning of the IC equipment at the VTT's CNS laboratory, the analysis method for analysing the total inorganic carbon and organic carbon in the sample solutions will be tested and developed. Sampling of the gas phase experiments will be started in 2021 and analytical method for analysing C-14 in the gas phase will also be studied during 2021.

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