CHANCE project

(Contract Number: 755371)

Report on study of the release behaviour of radiocarbon from another type of waste

DELIVERABLE (D5.6)

Work Package 5

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Contents

1. Objective

The aim of the CHANCE project was to develop methods for the characterisation of conditioned radioactive waste. While the focus of Task 5.2 was particularly in characterisation of outgassing of radiocarbon from graphite waste, additional experiments were also carried to evaluate the potential of cavity ring-down spectroscopy (CRDS) for the monitoring of radiocarbon outgassing from other types of nuclear waste.

Spent Ion Exchange Resin were selected for this task as it is a nuclear waste constantly produced during operation of nuclear power plants and is often problematic. Liquid processes and waste streams at nuclear facilities (e.g. reactor primary coolants or liquid radioactive waste management systems) require treatment to remove the main radioactive contaminants. Ion exchange resins are often used for this purpose. Spent resins are replaced regularly and are a form of low and intermediate level radioactive waste that must be treated and conditioned for storage and disposal purposes. One method can for example be to solidify this waste with cementation techniques. Such waste was available at VTT from its research reactor and could easily be studied in this project.

In a nuclear power plants, radiocarbon is mainly produced by the $^{14}N(n,p)^{14}C$ reaction from nitrogen by thermal neutrons from the reactor core as well as from ^{17}O and ^{13}C atoms via the $^{17}O(n,\alpha)^{14}C$ and $^{13}C(n,\gamma)^{14}C$ reactions. C14 is thus present for instance in the primary coolant system (originating from dissolved nitrogen and oxygen atoms) which is then filtered by the ion-exchange resin. C14 can therefore accumulate inside the resins and has then the potential for outgassing into $^{14}CO_2$ and organic molecules such as methane ($^{14}CH_4$).

2. Methods

2.1 Radiocarbon detection with cavity ring-down spectroscope

The detection of radiocarbon (C14) outgassing was based on the detection of $^{14}CO_2$ molecule P(20) absorption line at mid-infrared at 2209.109 cm^{-1}. The low absorption of the line because of low concentration of the $^{14}CO_2$ in the samples required using cavity ring-down spectroscopy to measure the concentration. Cavity ring-down spectroscopy is based on measuring decay time of light intensity between two high reflectivity mirrors. A laser light is coupled into a cavity formed by the two mirrors, resulting in light intensity build-up in the cavity. When light is switched off, the light intensity decays out exponentially, because of the loses in the mirrors. A gas, which absorbs light at the laser wavelength, results in a faster decay than in an empty cavity. The wavenumber dependent absorption coefficient at the measured wavelength can be calculated using the following equation: $\alpha(\nu) = 1/[c\tau(\nu)] - 1/[c\tau_0]$, where ν is the wavenumber and c is the speed of light. τ is the decay time of the exponential decay, known as the ring-down time, measured with sample in the cavity and τ_0 is the ring-down time in an empty cavity. Using the cavity ring-down spectroscopy, the optical pathlength in the gas can be maximised, which allows detection of even the lowest gas concentrations.

The cavity ring-down setup is shown in the Figure 1, and further details can be found in Ref [1]. In the setup, a L12004-2209H-C quantum cascade laser (QCL) from Hamamatsu with a central wavelength at 4.527 µm was used. The laser is guided through collimating lens, two optical isolators and two mode-matching mirrors to an optical cavity formed by two high-reflectivity ZnSe mirrors. The high-reflectivity mirrors have reflectivity of 99.97 % and 1 metre radius of curvature. The second mirror is mounted on a piezo-electric actuator-controlled platform. The cavity and the mirrors are enclosed inside an insulated and temperature-controlled cell, which has antireflective-coated CaF_2 windows for the laser entrance and exit. The low pressure required by the measurements is achieved with a scroll pump and the pressure is monitored with capacitance manometer. After the second mirror the light is guided to a photovoltaic detector and the detector signal is recorded by a FPGA card. The signal is processed and analysed with a LabVIEW-based software. By simultaneously scanning the cavity length with the mirror on the piezo mount, and scanning the laser wavelength, an absorption spectrum of the scanned laser range is formed. The spectroscope is positioned to a moveable 19-inch instrument rack.

The concentration of the radiocarbon was determined by fitting a sum of Voigt profiles with a non-linear least-square fitting routine to the measured absorption spectra, which were first smoothed with a moving-average filter. To obtain the radiocarbon concentration, the total CO_2 concentration in the cavity needed to be measured. This was done by measuring a $^{13}CO_2$ line at 2209.77 cm^{-1} with the CRDS and using the same line fitting method as for the radiocarbon spectra. The concentration of i = C14 or i = CO_2 is calculated from the absorption line area using equation: $C_i = (A_i k_b T)/(S_{oi} p)$, where A_i is the absorption line area, k_b is the Boltzmann constant, T is the sample temperature, S_{oi} is the absorption line strength and p is the sample pressure. The $^{14}C/^{12}C$ concentration was calculated as C_{C14}/C_{CO2} ratio.

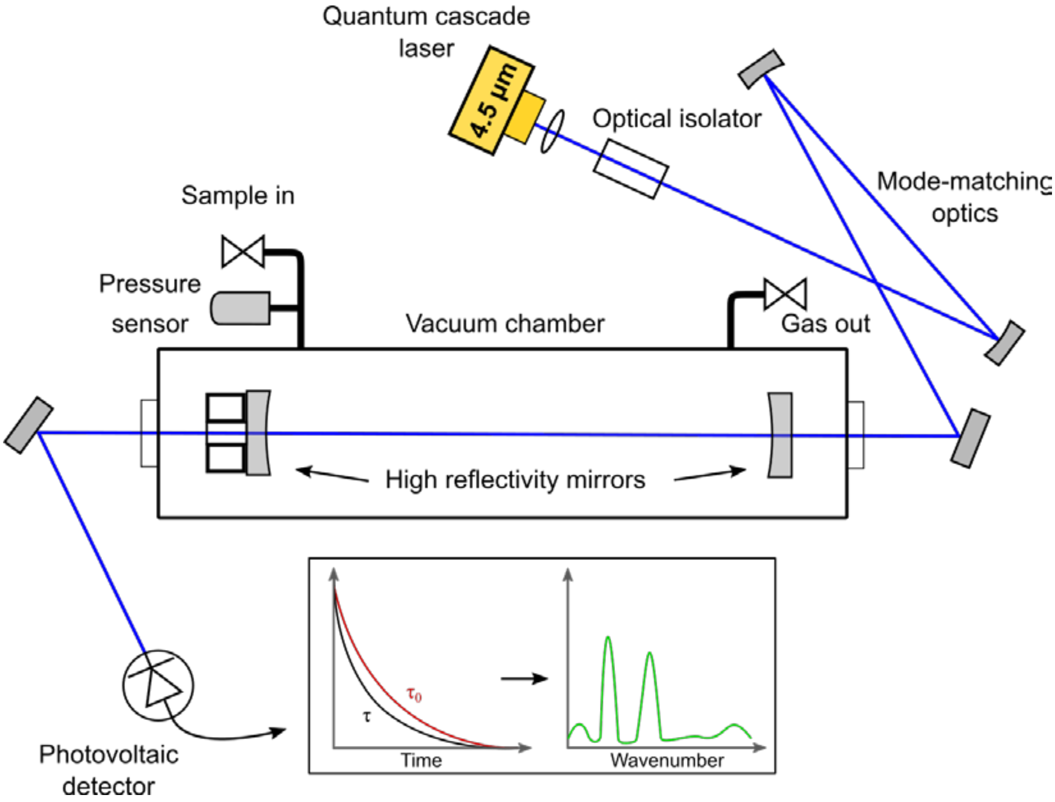

Figure 1. Schematic of the CRDS arrangement used for C14 outgassing measurements.

2.2 Sample processing unit

The CRDS measurement requires concentrating the CO_2 to enable detection of low C14 concentrations at good accuracy. Therefore, an on-line sample processing unit was built for the CO_2 purification and used together with the CRDS. The sample processing unit is shown in Figure 2, and detailed information of the sample processing unit is given in Ref [1].

The sample processing unit takes in samples in gas phase. A diaphragm pump is used to flow the air through the sample processing unit. The gas flows through a particle filter to a catalyser, which converts methane and other hydrocarbons to CO_2. The conversion occurs on palladium catalyst which is kept at 500 °C temperature. The preparation of catalyst is presented in more detail in Ref [2]. Conversion of hydrocarbons to CO_2 allows detecting C14 also originally present in other molecular species than CO_2 (such as methane). The catalyser can also be bypassed to get the C14 content only in CO_2. After the catalyser, a Vaisala GMP343 carbon dioxide sensor is used together with a pressure sensor to detect the CO_2 content in the sample air. A mass flow controller adjusts the flow speed, and solenoid valves guide the sample flow to one of two identical CO_2 traps. The two traps are used sequentially so, that when one trap is releasing trapped CO_2, the sample air is flown through the other trap that collects new CO_2 sample. The traps are made of aluminium blocks made into form of heat sinks. The trapping material, Lewatit VP OC 1065 ion-exchange resin from Lanxess, is positioned inside a drill hole made into the blocks. The resin adsorbs CO_2 selectively from air at room temperature. The CO_2 is released to the CRDS cell from the resin by heating the trap over 50 °C temperature. The heating is achieved with resistive heaters. After the CO_2 release, the trap is cooled back to room temperature with fans. The trapping time depends on the CO_2 concentration of the sample air, but typically 30 minutes was the minimum time to gather enough CO_2 for the CRDS measurement.

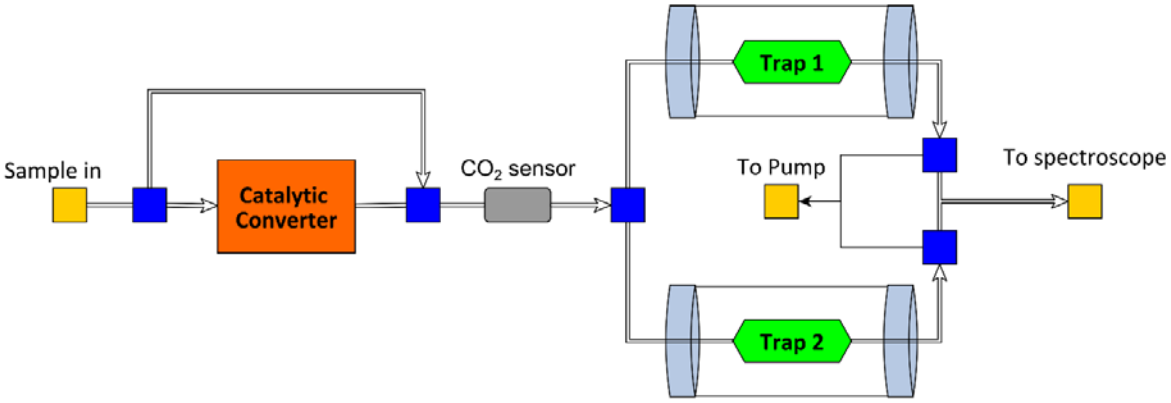

Figure 2. Schematic illustration of the sample processing unit.

In order to accelerate the outgassing of the spent resin, the samples were placed in custom-made oven. By flowing a constant flow of synthetic air at mass flow of 0.40 l/min through the oven shown in Figure 3, C14 was oxidised into carbon dioxide and could then be measured by CRDS. The oven can be heated up to 600 °C and the cylinder containing the samples can easily be replaced in case of contamination. Several temperature sensors are placed in the system, e.g. at the inlets and outlets, to monitor the temperature of the oven. The oven outlet was connected directly to the inlet of the sampling unit described in Figure 2.

Figure 3 : compact oven designed to enhance the outgassing and for rapid characterisation of the C14 content after full oxidation into carbon dioxide.

The resin samples used here originate from VTT FiR1 research reactor. The resins were taken from the columns into plastic barrels and let to air to dry until most of the water had evaporated. The barrels were then closed and kept in room temperature for several years before analysis. The resin was an Amberlite IRN150, which is a 50:50 mix of the IRN77 and IRN78 types. It has a particle size of 650 µm. Figure 4 shows an example photograph of one resin sample. The resin C14 concentration had been determined earlier using liquid scintillation counting, two different resins samples were studied here (labelled here *sample 002* and *sample 005*). The C14 activity concentrations were for sample 002: 176.3 Bq/g and for sample 005: 33.6 Bq/g. Samples of 0.109 – 0.409 g were taken from the resins for the combustion experiments.

Figure 4. Samples of spent ion-exchange resins used for the measurements. The photo of the resin on the right is taken after partial combustion with the oven and some blackening of the resin can be seen.

3. Results

The resin sample was placed in the oven with a slowly increasing temperature. The amount of CO_2 outgassing was monitored using a CO_2 sensor. Figure 5 shows an example of the CO_2 production dependence on the temperature of the oven. 0.2 g of resin 002 was weighted to the oven and the CO_2 outgassing was trapped for the whole time of the outgassing to one CO_2 trap. Note that the oven itself reached a temperature of 200 °C, but the temperature of the sample did not reach the same temperature, because of the continuous air flow. The CO_2 outgassing starts around 100 °C and reaches a maximum at 160 °C. This temperature was selected for this experiment such that sufficient CO_2 is released for the subsequent trapping such that the trapping time is not too long. After that the CO_2 output decreases. This is due to the fact that the temperature is not high enough to ignite the sample for complete combustion, but oxidation of most reactive molecular species occurs at low rate on the resin surfaces. The CO_2 outgassing drops as the reactive species are being consumed. After the combustion experiment at 200 C, 0.123 g of resin was left unburned.

Note that the combustion process occurring in the oven oxidised the produced gases, convert all the C14 species into CO2. This allows the determination of the total amount of C14. However, it also means that it is not possible to analyse the C14 speciation with this approach.

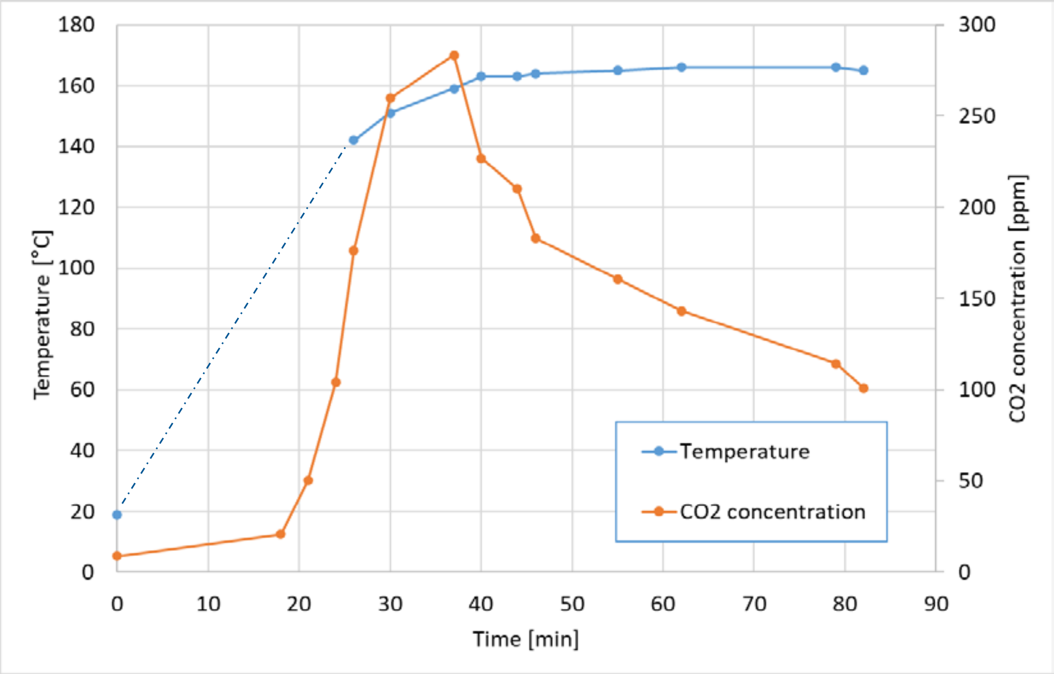

Figure 5 : CO_2 output from the combustion of the spent resin as function of oven temperature.

Once sufficient amount of CO_2 is produced, trapping using the sample processing unit and analysis of the C14 amount with CRDS was carried out. An example of such a measurement is shown in Figure 6. Elevated levels of C14 were detected after partial combustion of the resin. 7.6 ppb of C14 was detected. This shows that C14 can easily be detected using CRDS, even though the activity of resin 005 was not very high (33.6 Bq/g). In a similar combustion up to 200 °C with resin 002, 35.1 ppb of C14 was detected with the CRDS. The ratio of CRDS measured C14 concentrations of the two samples *7.6 ppb / 35.1 ppb = 0.217* is close to the ratio of activity concentrations *33.6 Bq/g / 176. 3Bq/g = 0.190* detected with LSC, which supports the validity of the CRDS method. In addition to CO_2, N_2O was also observed (lines on each side of the $^{14}CO_2$ line). In fact, after complete combustion of a resin sample, the increased N_2O concentration prevented the detection of C-14. In this experimental configuration, a temperature of 200 °C was used even though a higher combustion temperature would possibly provide a more complete combustion. This temperature was selected for two reasons: first the oven was designed to be simple and compact in order to maintain the advantage of the optical detection method used here. In this first prototype higher temperatures would not have been stable, also requiring additional heating capacities. Secondly, it was observed that higher temperatures resulted in higher concentrations of N_2O preventing the sensitive detection of C14. However, the outgassing of N_2O increased with the oven temperature. Combustion of sample 002 at maximum temperature of 190 °C resulted in lower N_2O concentration ($[N_2O] = 41.8$ ppm) measured by CRDS than during the combustion up to 200 °C ($[N_2O] = 56.6$ppm) or 220 °C ($[N_2O] = 79.4$ ppm), even though the sample mass was largest in the combustion at 190 °C. The reason for increased N_2O outgassing is not yet fully known. However, some hypotheses can be formulated. Even though combustion of the spent resin will certainly release large amount of N_2O (e.g., through the degradation of functional groups of the ion-exchange resins or nitrate ions that could be present in the ions exchange resins), the subsequent CO_2 trapping resin should selectively trap only CO_2 and not N_2O. It was however observed that the trapping resins also release N_2O when heated. Releases from the combustion of spent resins might further degrade the trapping resin, and when this occurs it results in an increased amount of N_2O when the trapping resin is heated.

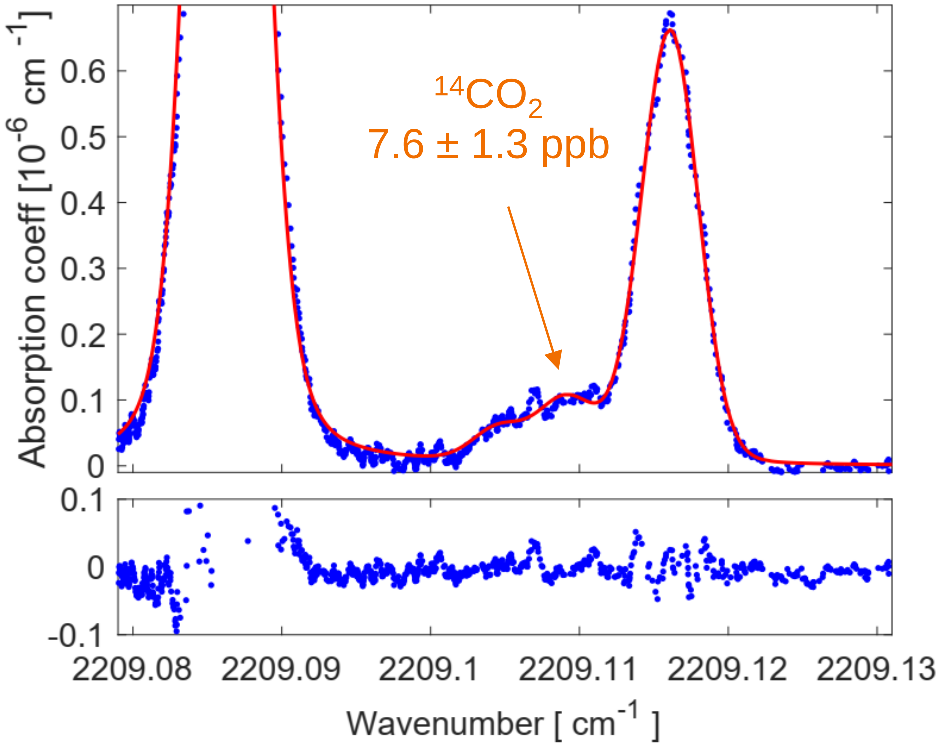

Figure 6 : Spectrum recorded with CRDS at a pressure of 3 mbar after partial combustion of a spent resin sample. The $^{14}CO_2$ absorption peak is visible at 2209.109 cm^{-1} and its strength corresponds to 7.6 ppb of C14.

4. Conclusion

CRDS was used successfully to measure the production of C14 production from spent ion-exchange resins. The method was able to detect small amount of C14 in real-time using a compact method. The probable presence of other radionuclides such as tritium did not interfere with the measurement. Apart from outgassing monitoring, we envision that the method can also be used for rapid characterisation of the C14 content for such waste. After full combustion the full amount of C14 can be determined. Thanks to the compact oven designed in this project and other compact components, the rapid characterisation can be performed directly on-site. C14 outgassing from irradiated graphite was also studied with CRDS and already reported in deliverable D5.4. This work therefore highlights that CRDS is suitable to determine the amount of C14 outgassing as well as the total amount of C14 in the sample for a variety of nuclear waste.

5. References

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