



## CHANCE project

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# Outlook on the prospects of using CRDS for HCl-36 outgassing measurement

DELIVERABLE (D5.3)

Work Package 5

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### 1. Introduction

The CHANCE project aims to address the specific issue of the characterization of conditioned radioactive waste. The characterization of fully or partly conditioned radioactive waste is a specific issue because unlike for raw waste, its characterization is more complex and therefore requires more advanced non-destructive techniques and methodologies.

The first objective of the CHANCE project is to establish at the European level a comprehensive understanding of current conditioned radioactive waste characterization and quality control schemes across the variety of different national radioactive waste management programmes, based on inputs from end-users members such as Waste Management Organizations and storage operators.

The second objective of CHANCE is to further develop, test and validate techniques already identified that will improve the characterization of conditioned radioactive waste, namely those that cannot easily be dealt with using conventional methods. Specifically, the work on conditioned radioactive waste characterization technology will focus on:

- Calorimetry as an innovative non-destructive technique to reduce uncertainties on the inventory of radionuclides;
- Muon Tomography to address the specific issue of non-destructive control of the content of large volume nuclear waste;
- Cavity Ring-Down Spectroscopy (CRDS) as an innovative technique to characterize outgassing of radioactive waste.

The present report focuses on activities from Work Package 5 related to the development of the CRDS for the detection of radioactive gases. Based on the different investigations carried out during the project, we evaluate the potential for HCl-36 detection with optical methods, such as CRDS. In addition, the potential of other methods such as ICP-MS is also discussed. In CHANCE a particular focus is given to the outgassing study of irradiated graphite.

Chlorine has two stable isotopes, Cl-35 and Cl-37, with natural abundances of 75.76 % and 24.24 %, respectively, and one long-lived radioactive isotope, Cl-36, with a half-life of (301000 years). During reactor operation, the main part of Cl-35 is activated into Cl-36 (Brown 1999, Colle 2002), through the reaction  $^{35}\text{Cl}(n,\gamma)^{36}\text{Cl}$ , which is characterized by a high cross section of 43.63 barn. Thus, even trace amounts of Cl-35 in nuclear fuel and any structural reactor material are sufficient to produce significant amounts of Cl-36, provided that there is a sufficient flux of thermal neutrons. Cl-36 in used fuel has for instance been measured (Sheppard *et al.*, 1996). Metallic material such as steel, aluminium or lead also contain chlorine impurities and are extensively in nuclear reactors, thus resulting in Cl-36 production (Parry *et al.*, 1997). Large volume of heavy concrete and graphite (in case of graphite-moderated reactors) will also lead to relatively larger amount of Cl-36 (Hou *et al.*, 2007).

Similarly, to C-14 and tritium, it also has potential for gaseous release during dismantling of nuclear facilities and storage of nuclear waste. However, it is most problematic in case of liquid discharges. Chlorine can be highly soluble in water and is thus mobile in the environment. Reactor water also contains Cl-36, originating from the chlorine impurities and leached from the reactor materials. High Cl-36 activity has also been found in ion-exchange resins, concentrated from the reactor water (Hou *et al.*, 2007). The high solubility also means that a significant dose peak occurs when water ingress into the site (Toulhoat 2007).

## 2. Nuclear Graphite

Nuclear graphite contains small amounts of impurities such as oxygen, hydrogen, metals and halogens, and chlorine. Chlorine contents varies from a few ppm to around 50 at ppm. Cl-36 release into water will depend on water saturation or water access into the graphite pores. In addition, the solubility of Cl-36 also depends on its physical and chemical properties, such as chemical form and diffusion and retention properties. The graphite porosity has a high influence on the chlorine release. Its microstructure is characterized by open porosity (OP - pore structures connected to the surface of the graphite) and closed porosity (CP - pore structures

isolated from the graphite surface). CP can be transformed into OP by oxidation of graphite and chemical species contained in it can be released after a certain time. Cl-35 in the OP is released relatively quickly at operating temperature, therefore only a very small fraction of the chlorine located in the initially open porosity can be activated; on the contrary, the Cl-35 located in the initially CP, can potentially reside in the flux for a considerable period, and thus undergo greater activation. The length of residence in the flux, and hence the quantity of Cl-36 released from the graphite, will therefore depend critically upon the rate at which CP is converted in OP. Experimental data suggests that closed porosity is accessed faster in the earlier stages of radiolytic oxidation than in the later.

The Nirex model was for example used to calculate the maximum ILW inventory of Cl-36 present in the irradiated graphite taking into account the release of Cl-35 and Cl-36 (Figure 1). It assumes that closed porosity is converted to open porosity at a constant rate throughout the life of the plant and chlorine release can be estimated for different porosity scenarios (Figure 2).

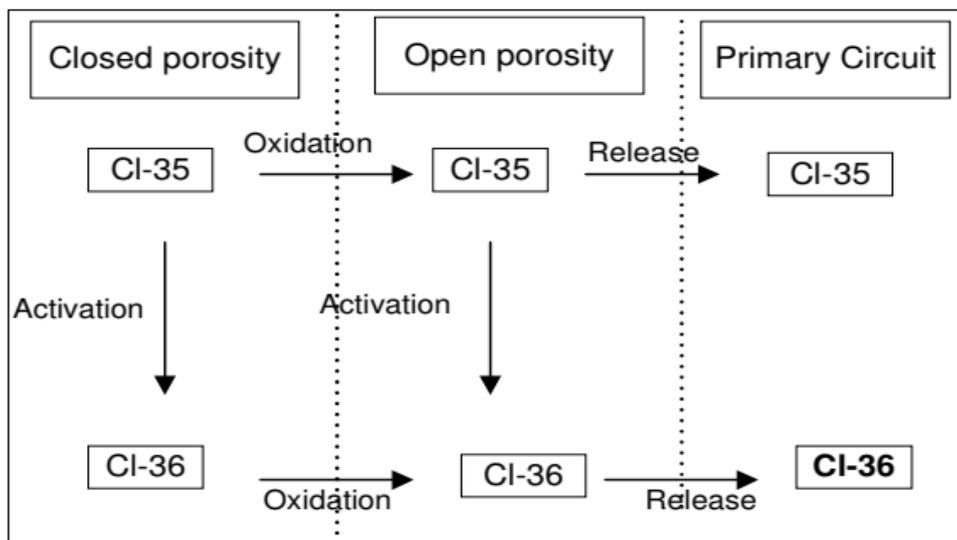


Figure 1 : Schematic of the Nirex Model.

Under reactor conditions, a large part of all chlorine isotopes is released instantly from that part of graphite porosity which is accessible to the coolant; Cl-36 generation take place only in CP; As CP is converted in OP, Cl-35 and formed Cl-36, are released almost instantaneously. 50% of Cl is thus removed from graphite within few hours when it heats up during the start-up of the reactor. The rest of chlorine is removed during the lifetime of the reactor. After dismantling

graphite waste therefore does not contain significant amounts of Cl-36. For this reason, the content of Cl-36 in the actual waste has often been overestimated.

Loss of chlorine due to different porosities can be calculated using these calculations:

Loss of Cl-35 from the opening of closed porosity (CPV)

$$dC/dt = dC/d\varepsilon \times d\varepsilon/dt \text{ hence: } dC/d\varepsilon = C/\varepsilon$$

C: Cl-35 concentration in CO (Atoms/m<sup>3</sup> graphite)

ε: CO volume (m<sup>3</sup> CO/m<sup>3</sup> graphite)

T: Time

Assuming that closed porosity is lost exponentially as a function of reactor life:

$$d\varepsilon/dt = -\beta\varepsilon \text{ hence: } dC/dt = -\beta C$$

$$\text{If } C = C_0 \text{ at } t = 0, \text{ then } C = C_0 \exp[-\beta t]$$

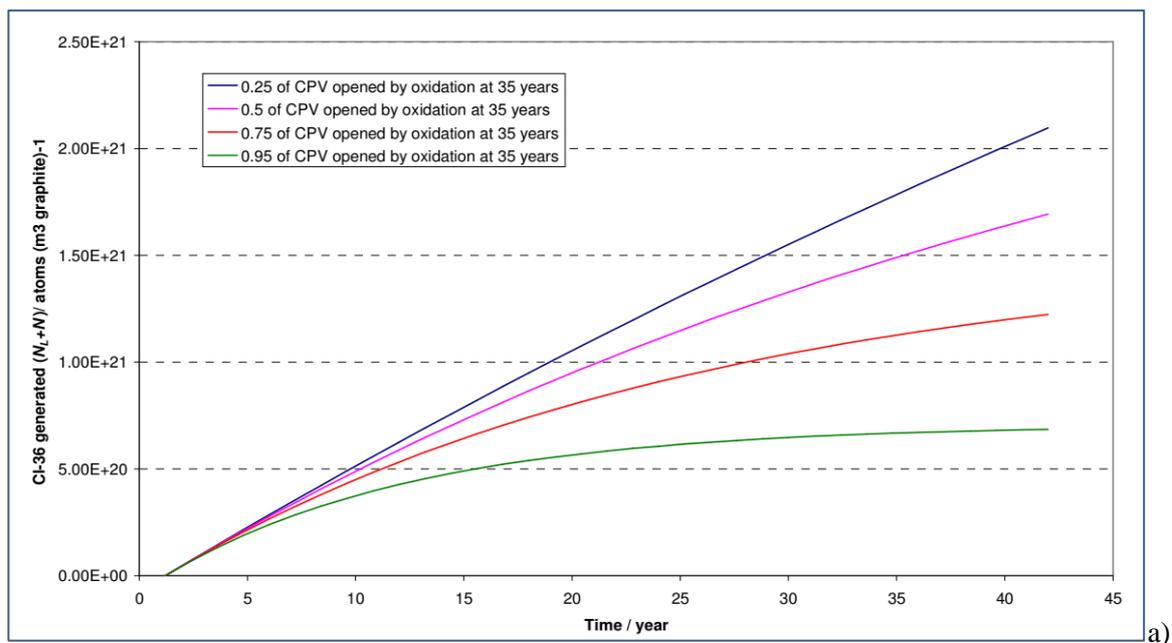
Cl-36 in irradiated graphite as a function of time

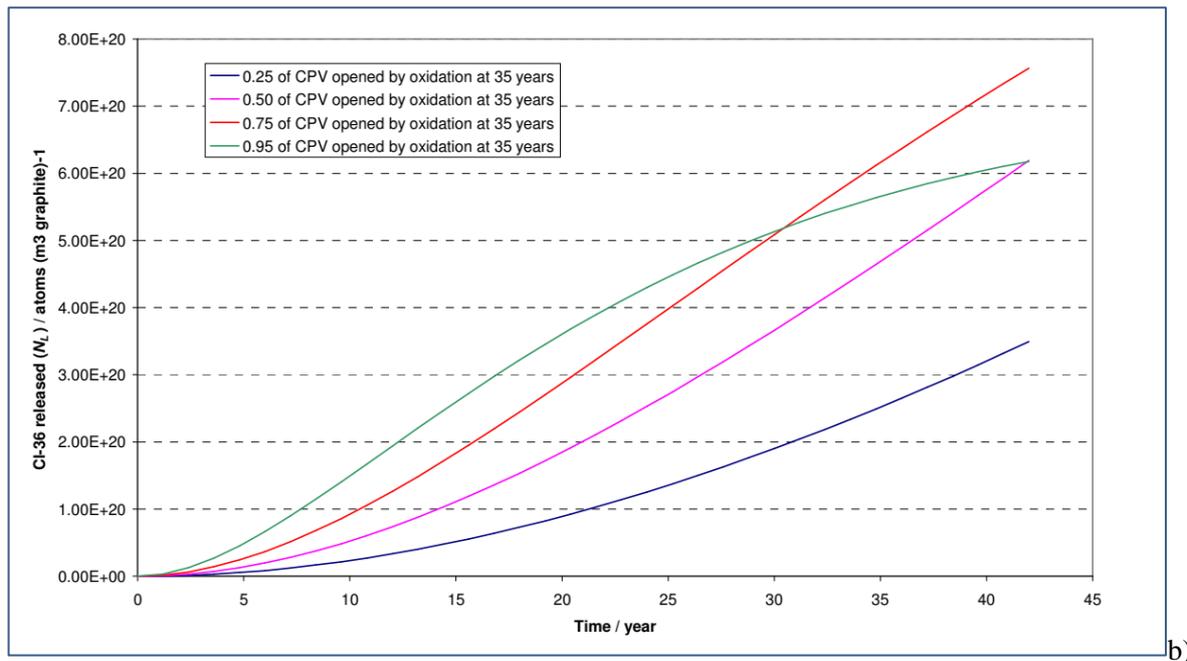
Assuming that the loss of Cl-36 by radioactive decay is negligible, and that only a small fraction of the available Cl-35 undergoes activation, if N is the number of Cl-36 atoms per m<sup>3</sup> of graphite:

$$dN/dt = kC - \beta N = kC_0 \exp[-\beta t] - \beta N$$

Where k = atoms of Cl-36 generated per atom of Cl-35 per unit time.

$$\text{If } N=0 \text{ at } t=0, \text{ then: } N = kC_0 t \exp[-\beta t]$$





**Figure 2 :** Predicted amount of Cl-36: a) total Cl-36 generated in graphite per m<sup>3</sup> graphite at different CP Volume opened; b) cumulative Cl-36 releases from graphite at different CP Volume opened.

### 3. Gaseous releases of Cl-36

Gaseous release of chlorine from graphite was studied by Vaudey et al. (2010). In particular, desorption of different molecules was investigated as function of temperature. As seen in Figure 3, the different volatile compounds will be released in different amounts. The desorption of HCl is the smallest, at rate 200 times smaller than carbon dioxide. The physical structure of the graphite (orientation of the grains) also influences the desorption. Note also that significant releases only occur at high temperature, above 170 °C. However, release at room temperature over several 10's of years as would occur in a repository is not negligible.

Vaudey et al. (2010) also studied the chlorine speciation, and it was determined that all the chlorine is released in the form of HCl (and not Cl<sub>2</sub>). Considering the use of the laser spectroscopy for chlorine detection, detection of HCl is easier than Cl<sub>2</sub>, as HCl has stronger absorption lines. However, HCl detection is also challenging as it is a very reactive gas, easily adsorbing on all surfaces.

An estimate of the expected total HCl release can be:

- Assuming a total Cl concentration in graphite value of 50 ppm;
- A maximum amount of 400 Bq/g of Cl-36 has been reported, which correspond to 300 ppb of Cl-36;

- One will then obtain a  $Cl-36/Cl_{total} = 0.6\%$ , which can easily be measured using laser spectroscopy, if one captures only and only the Cl-gas (HCl gas);
- Using a minimum value of Cl-36 in graphite as 4 ppt, one gets  $Cl-36/Cl_{tot} = 80$  ppb, which is measurable with CRDS.

This calculation assumes that all of the HCl is eventually released into HCl. As the release of HCl (at least at room temperature) is very small, heating of the samples is necessary to generate enough sample to fill the measurement cavity and allows the measurement. As shown in Figure 3, other gaseous species will be release in much larger amounts which will dilute the HCl and there is therefore no real alternative to concentrating the HCl using a trapping method.

#### 4. Detection with laser spectroscopy

As discussed in deliverable D5.2, a CRDS system built for HCl detection can achieve a limit of detection of 1 ppb (in the near-infrared) or even 0.1 ppb (in the mid-infrared wavelength region). Those limits are assuming no significant interferences from other species such as water. As discussed earlier, CRDS will be suitable of HCl monitoring assuming that HCl can be purified and almost pure HCl can be directed into the measurement cell.

If HCl can be trapped efficiently it is clearly feasible to detect it with HCl. If the HCl can be collected from and purified this will enhance the measurement sensitivity. While purification of HCl is challenging due to its highly reactive nature, we can describe here a few possible approaches.

HCl can be trapped in a liquid medium using a bubbler and subsequently release by heating up the liquid sample. However, one has to consider also interfering species such as water which can interfere with the measurement due to overlapping absorption lines (as described in D.5.1). Other liquid trapping media than water can also be considered in order if it has less interfering lines. Note that by using the mid-infrared range for HCl-36 detection, interference from water vapour can also be minimised as described in D.5.2.

Alternatively other trapping methods can be explored where trapping into a liquid medium is not required. A cryogenic trap can be used to concentrate HCl below its boiling point ( $-85\text{ }^{\circ}\text{C}$ ) and then release it by heating the trap, as shown schematically shown in Figure 4. A similar system for  $\text{CO}_2$  is for instance described in Genoud *et al.* With such an approach high concentration of HCl can possibly be achieved. An adsorbent material can be used to trap HCl and subsequently release it.

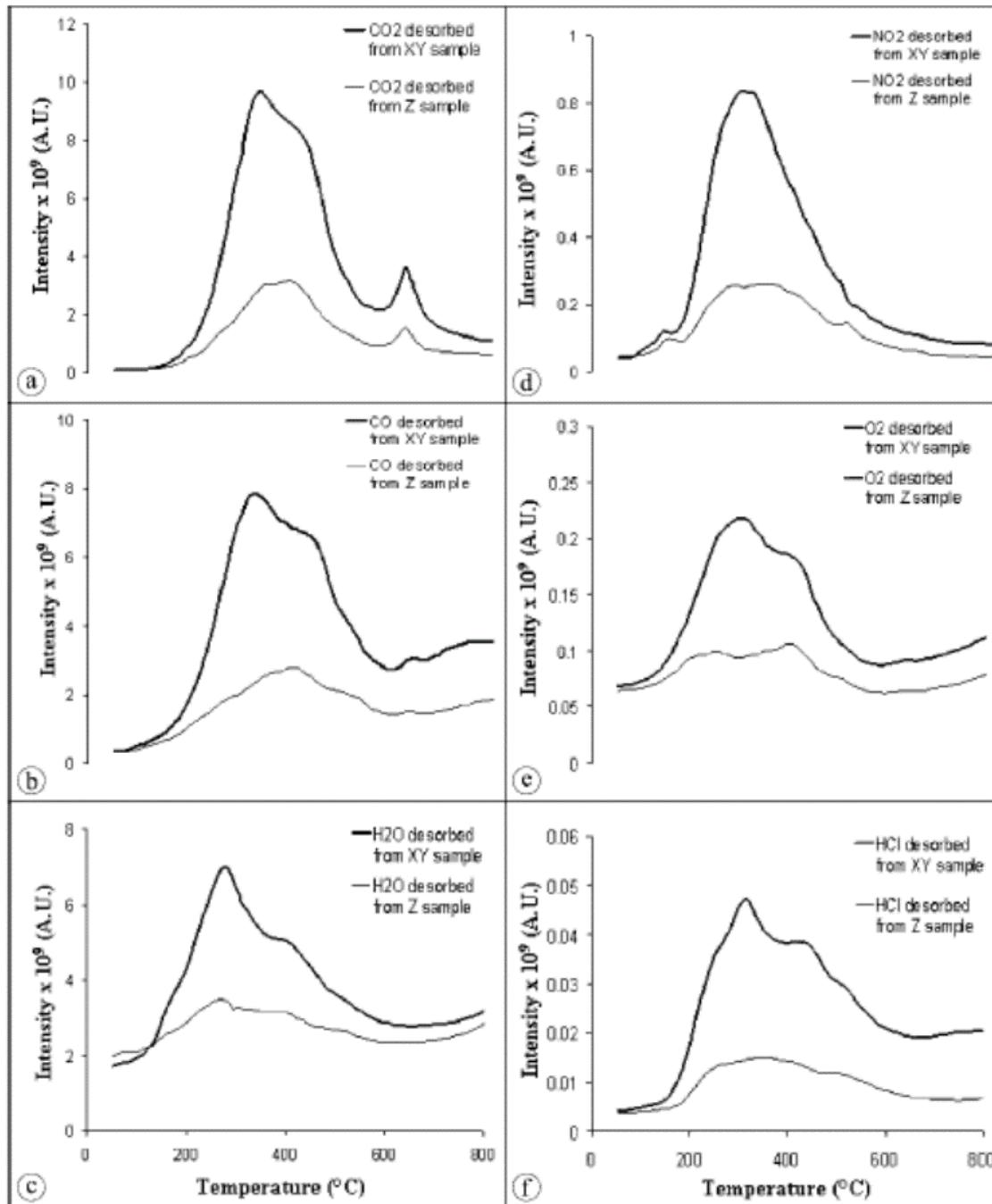


Figure 3 : Quantities of (a) carbon dioxide, (b) carbon monoxide, (c) water, (d) nitrogen oxide, (e) oxygen and (f) hydrogen chloride desorbed from virgin nuclear graphite for XY (grains preferentially oriented perpendicularly to the spinning axis) and Z (grains preferentially oriented along to the spinning axis) samples monitored using temperature-programmed desorption. Figure from Vaudey et al. (2010).

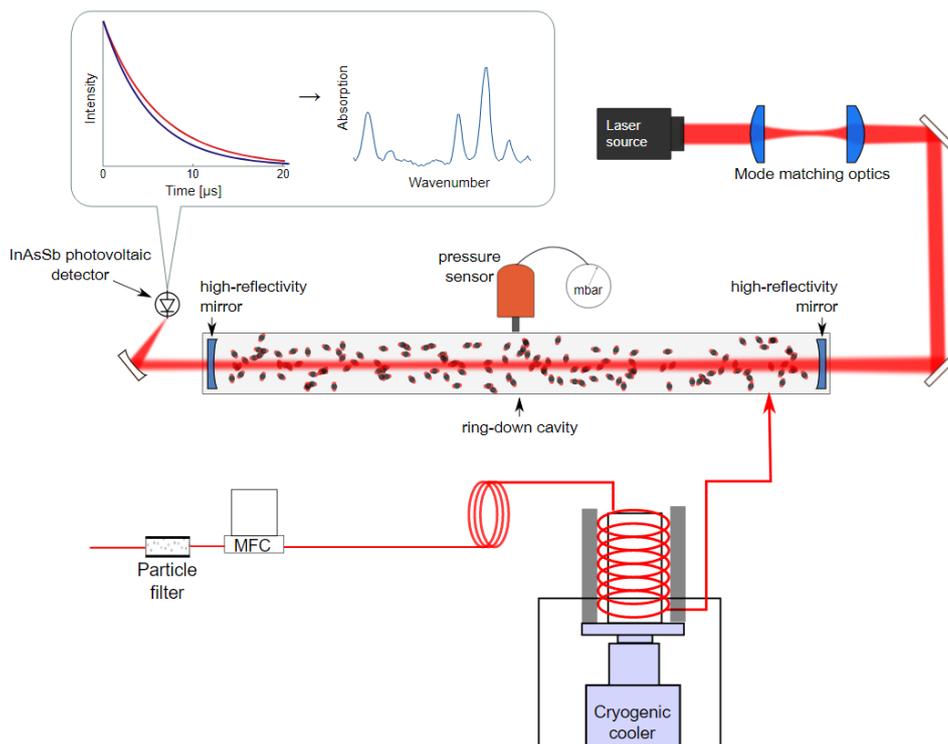


Figure 4 : schematic view of a possible HCl trapping system connected to a CRDS instrument.

## 5. Analysis of chlorine gases released from irradiated graphite using other methods

Other methods than laser spectroscopy was also studied in this project. For determination of the Cl-36 concentration in samples of irradiated-graphite, chemical methods are generally applied. They were based on the sample decomposition by acid digestion. The sample is put into a digestion system. A certain mixture of acids ( $H_2SO_4 : HNO_3 : HClO_4 = 15 : 4 : 1$ ) is added to the sample, later it is heated to 150-200°C for several hours or days. Chlorine is released from the sample as HCl and  $Cl_2$ . Cl-36 can be isolated as AgCl and purified using ion-exchange chromatography. Finally, it can be determined by Liquid Scintillation counter (LSC). The main limitations are that only very small sample quantities can be treated in this way, leading to possible underestimates of the real chlorine content. Furthermore, this method is not sensitive to other gases that may contain active isotopes.

A new approach would be to sample directly the gas released from graphite. A piece of irradiated graphite is placed in controlled vacuum conditions and at a given temperature for a desired time. Depending on the temperature (which can simulate the working temperature of the repository conditions), the gas can be released. In a subsequent step, the released gases can

be transported by a flow of a carrier gas to the analyzers for CO<sub>2</sub>, <sup>13</sup>C and <sup>14</sup>C content (by Cavity Ring Down laser Spectroscopy) and then to the beta spectrometer (Liquid Scintillation Counting) and to the mass spectrometer ICP-QMS for total Cl and <sup>36</sup>Cl content, using H<sub>2</sub> injected in the collision cell (Figure 3). In this way we can study the effects of different parameters, such as time, temperature, and environmental pressure on the release of gases from graphite. In principle, through the use of cold traps or chemical traps, different types of released gas (for instance CO<sub>2</sub>, Cl<sub>2</sub> and HCl) can be separated.

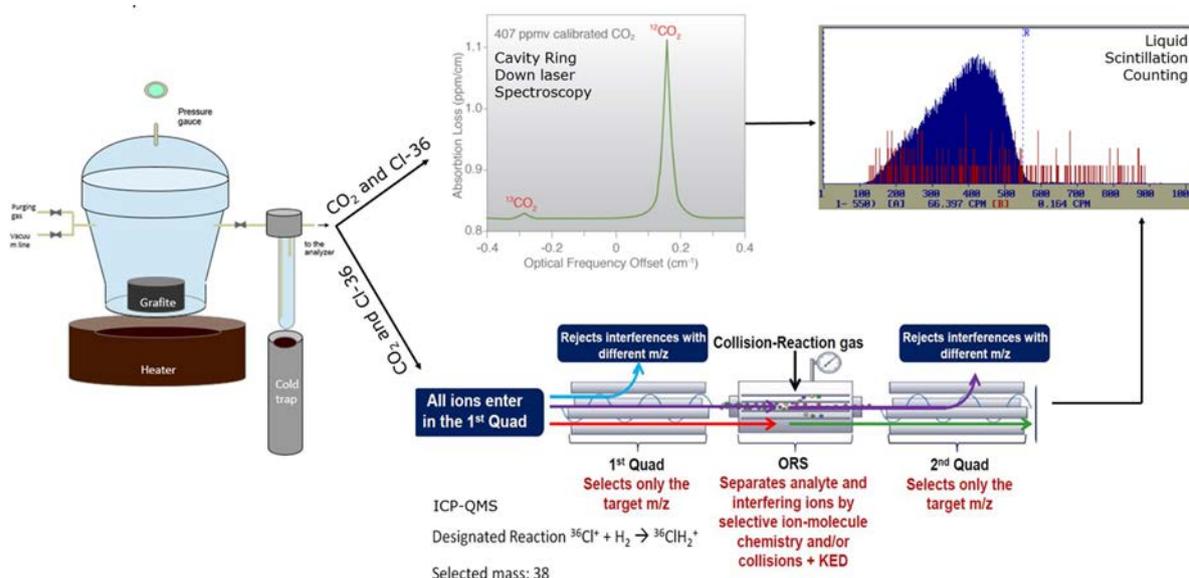


Figure 5 : Proposed method to analyze gases released from irradiated graphite.

### 5.1 Development of HCl-36 measurement with ICP-MS-QQQ

Stable Cl-35 has been successfully measured by ICP-MS-QQQ (triple quadrupole (Nakano, 2018; Nelson, 2019). As described in Russel et al. (2021), the main interference of concern is polyatomic <sup>16</sup>O<sup>18</sup>O<sup>1</sup>H, which can be overcome using a sequential reaction with H<sub>2</sub> to shift Cl-35 to <sup>35</sup>Cl<sup>1</sup>H and then to <sup>35</sup>Cl<sup>1</sup>H<sub>2</sub>, whilst the reaction with <sup>16</sup>O<sup>18</sup>O<sup>1</sup>H does not proceed.

As better described in literature, the Limit of Detection (LOD) for ICP-MS measurement for stable Cl was 0.01 mg kg<sup>-1</sup>. Equivalent to 12.2 Bq kg<sup>-1</sup> Cl-36. The specific activity of Cl-36 (1.07 10<sup>9</sup> Bq g<sup>-1</sup>) potentially allows mass spectrometric measurement. There are few scientific papers related to ICP-MS procedure for measurement of Cl-36. For example, Russel et al.

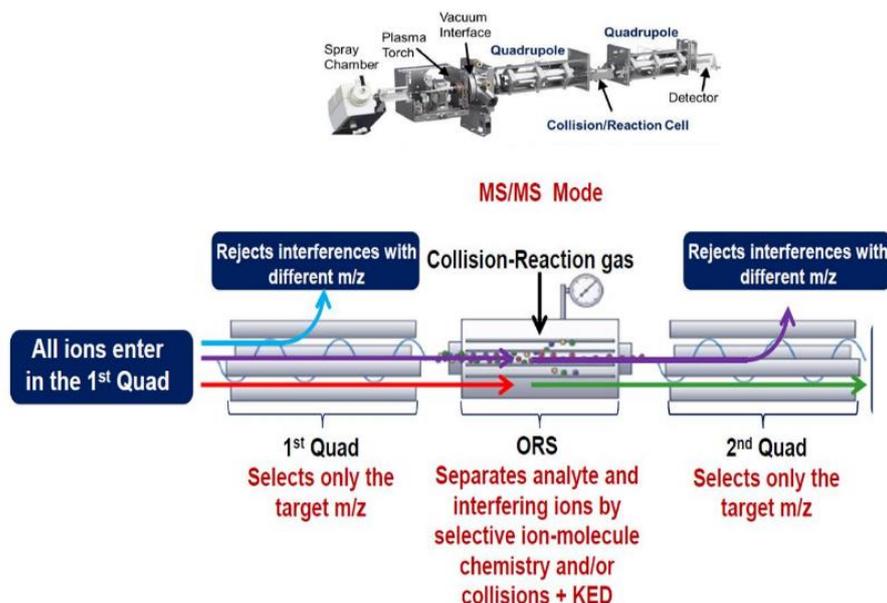
(2021), described the procedure used to detect Cl-36 using an ICP-MS-QQQ 8800 Agilent, that is the same instrument present at the ENEA Laboratory.

As for Russell et al. (2021), we detect Cl-36 using hydrogen as collision gas in the collision/reaction cell (CRC), because using the other gas available the Cl-36 data obtained are not good. Samples were measured using two different solutions:

- First test with NaCl (Sigma Aldrich – not ultrapure) solubilized in HNO<sub>3</sub> 3% for trace analysis.
- Second test with KCl (Sigma Aldrich – suprapure) with Sr(NO<sub>3</sub>)<sub>2</sub> (Sigma Aldrich) in the same quantity to evaluate the different analysis efficiency between the halogen and the alkaline earth metal.

Both the tests have been carried out using a standard solution without chlorine (B0 solution) and the setup schematically shown in Figure 4. The instrument was first conditioned with B0 solution for different hours. Between the two tests, the second test with KCl shows good results.

**A sensitivity of around 10 ppm represents the limit of detection (LOD) for the Cl-35 detection.** The results for stable Cl highlight the potential for measurement of radioactive Cl-36, not previously measured by ICP-MS.



**Figure 6 :** Schematic of the ICP-MS in MS/MS mode with reaction cell operating.

## 6. Conclusion

We have shown that HCl-36 detection is possible with laser spectroscopy as suitable absorption lines were experimentally measured (D5.2). In this report, a strategy for the development of a more advanced laser spectroscopy system (e.g., CRDS) capable of detecting trace amount of HCl-36 is outlined, also taking into consideration sampling issues. More research work is however required to achieve this goal, which is particularly challenging due to the low concentration of Cl-36 expected in the outgasses from, e.g., irradiated graphite waste. The reactive nature of HCl will pose several issues that need to be addressed to provide reliable measurements. The use of ICP-MS for Cl-36 detection has also been explored and can in the future complement optical detection methods.

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