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Decontamination Factors by Steam Reforming

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Decontamination Factors by Steam Reforming

Executive summary

Thermal Treatments with water steam (TTWS) have been evaluated as a possible option for i-graphite decontamination. Several experiments have been performed with both virgin and irradiated graphite, in particular considering DIDO, MERLIN and Saint Laurent A2 graphite. The main reaction taking place at temperatures higher than 800 °C is the water gas one, but the shift reaction cannot be excluded completely since the facilities were not designed taking into account possible secondary gas-phase reactions; however, the majority of the gases revealed to be CO and H_2. The continuous provision of small quantities of water vapour revealed an increase both of the radionuclide removal and the mass loss during treatment: the amount of water vapour has been optimized for the present work to 10 g/kg by using specimens of virgin graphite. Several treatments have been established with a temperature of 1000 °C and 10 g/kg absolute humidity.
TTWS revealed higher Decontamination Factors (DFs) than other treatments (using inert gas) and lower mass losses compared to thermal treatments with oxygen. Tritium removal is probably enhanced due to isotope exchange reaction(s), with DFs up to 13 for Merlin graphite and 2.27 for Saint Laurent A2 graphite, under the same conditions. Radiocarbon showed to be partially removed due to a less aggressive corrosion agent than oxygen, with DFs up to 1.4 and 1.08 respectively for Merlin and SLA2 graphite. It is observed, in general, that Merlin graphite is more efficiently decontaminated (from both H-3 and C-14) than SLA2 graphite: it has to be underlined, however, that SLA2 graphite already experienced significant mass losses due to radiolytic corrosion during reactor operation, so a fraction of the radionuclides could have been already removed in-situ.
TTWS seem to be promising for what concerns H-3 and C-14 removal, but some points have to be considered:

- A direct application of water steam during thermal treatment results in a dilution of H-3: a pre-roasting under inert gases is strongly recommended in order to remove Tritium as much as possible;
- The continuous provision of reactants to the graphite seems not to be effective enough to guarantee high decontamination factors for C-14. A multi-step treatment with reloading of reactants and application of high temperatures in separate steps could be a promising solution;
- Comparison of results coming from different institutes (EDF, SIA ´Radon´) underlined the necessity of understanding and considering the entire lifetime history of every i-graphite, leading at the end to different behaviours and results.

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1. Introduction

Graphite is a very important material in nuclear applications because of its physical properties and thermal and mechanical durability. Therefore it can be used as reflector, moderator, fuel matrix and construction material [FLO09] [POD04].

During the operation in nuclear reactors graphite gets irradiated and acquires radioactive materials. The acquired activity is high enough to declare nuclear graphite as nuclear waste. In Germany, the current waste-management strategy for carbonaceous radioactive is an optimized packing concept in deep geological formations [FAC08] [BfS]. The large volume of irradiated graphite and carbon bricks is reducing the cost efficiency of this strategy, because the bulk amount is inactive ^{12}C [FAC08]. Another problem is the content of longlived radioisotopes (e.g. ^{14}C, ^{36}Cl) [EUR08].

To find a solution to these waste and volume problems EURATOM proclaimed the project CARBOWASTE, which focuses on treatment and disposal of irradiated graphite and other carbonaceous waste.

Within the framework of CARBOWASTE Podruzhina's dissertation "Graphite as radioactive waste: Corrosion behavior under final repository conditions and thermal treatment" was one of the first showing that a steam reformation of graphite might work. Hence this work is based on Podruzhina's dissertation and focuses on the decontamination of irradiated nuclear graphite (i-graphite) by steam reforming.

The main objectives of this thesis were:

- performing a system test with tube furnace Carbolite STF 15/-/180 and carry out experiments with a connected humidity generator to gain knowledge about the treatment method of steam reforming with varying parameters of temperature, humidity and duration of treatment.
- determine decontamination factors concerning ^{3}H and ^{14}C of steam reformed irradiated nuclear graphite.

The further goal of these experiments on irradiated nuclear graphite is developing a prototype installation for the decontamination of graphite so the radioactive waste has a lower volume and eventually the graphite can be reused.

2. Graphite

Graphite is a natural occurring form of carbon. It builds flat layers with poly-cyclic rings of six carbon atoms. These parallel layers are bonded by weak van der Waals forces.

The layer distance is 335 pm, while carbon atoms between each other have a distance of 141.5 pm. Every carbon atom has a bond to three other carbon atoms via -bonding. Therefore one free electron is available to every carbon atom to build a delocalized π-bonding-system. These free electrons are responsible for graphite's good conductivity.

There are two different modifications of graphite due to different stratification:

- α-graphite (hexagonal crystallization)
- β-graphite (rhombohedral crystallization)

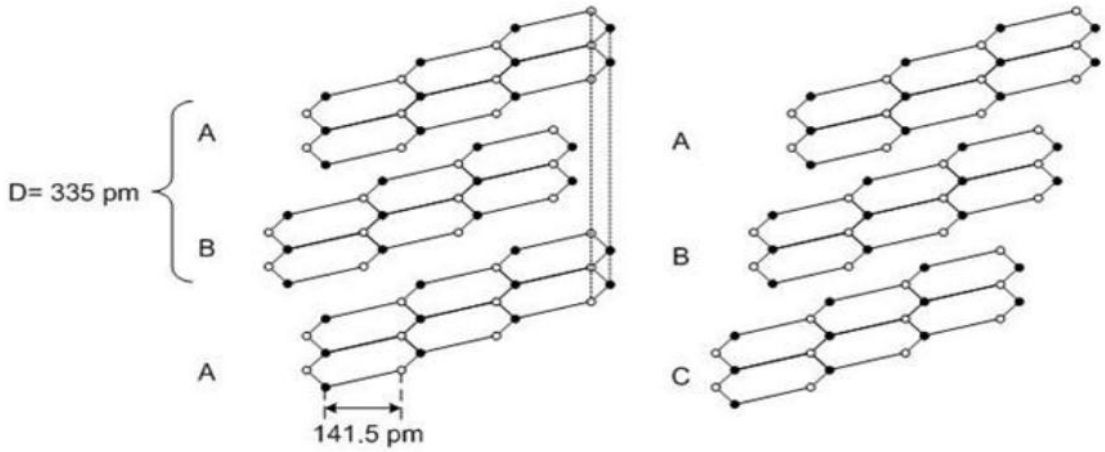

Figure 2.1: α-Graphite (left) and β-graphite (right) [FIS12]

2.1 Graphite in nuclear applications

Graphite was widely used within nuclear reactors till the 1990s. It is an important construction material in nuclear reactor design, because it retains its properties at high temperatures concerning [FLO09] [FIS12]:

- high resistance to thermal shocks
- good thermal conductivity
- low coefficient of thermal expansion
- low cross section of neutron absorption
- good mechanic machinability

Nuclear graphite in nuclear reactors needs to be free of boron or other neutron absorbing materials, because these would hinder a proper nuclear fission. Hence the content of neutron absorbing materials should be less than 5 ppm.

In Germany, nuclear graphite was used in the pebble bed reactors as construction material, reflector material and nuclear fuel coating. Another use of nuclear graphite is the Russian RBMK where it was used as a moderator.

In its natural form, graphite cannot be used for nuclear applications. It needs to be specifically manufactured according to its intended use.

The production of graphite consists building the “green body” (see below), pyrolyzing beneath 1300 °C, increasing of the density by impregnation and finally, graphitization at 2500 °C to enforce the binder’s crystallization.

The green body is a shapeable compound of coke grains and carbonaceous binders like pitch and tar. There are different methods of shaping and pressing to influence the conductivity of graphite, especially when it comes to the design of moderator and reflector materials.

A secondary pyrolysis at 1000 °C begins to extract the binders after the green body was molded; because of the pyrolysis carbon bridging occurs which leads to a homogeneous graphite mold. Subsequently, the graphite mold is covered with a carbonaceous impregnator to close the porosities. The final graphitization at 2500 °C to 3000 °C should cater for the crystallization. In this step, density is increased and impurities are removed. If coke grains are

not perfectly crystallized, there will be great discrepancies between the graphite layers which lead to a lower oxidation resistance within the mold.

Despite the previous mentioned production processes, the graphite mold still has a great number of porosities which are categorized by the following diameters according to [DEL83]:

- micropore: d < 2 nm
- mesopore: 2 nm < d < 50 nm
- macropore: 50 nm < d

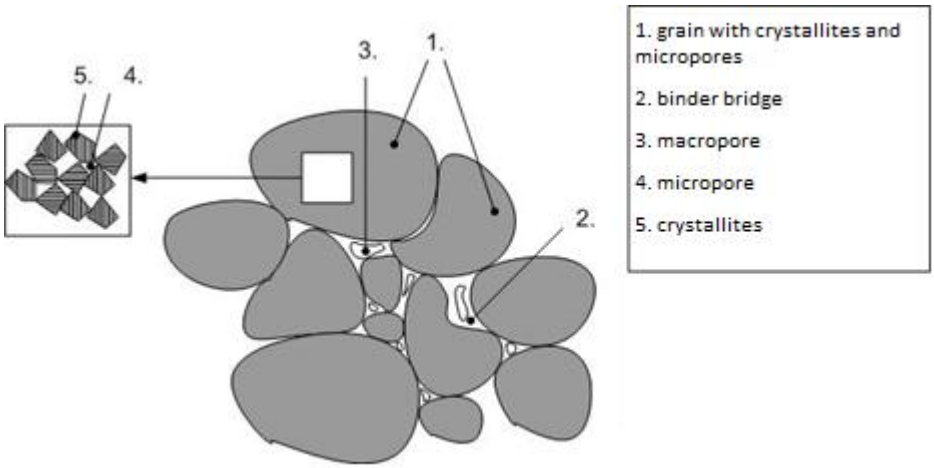

Figure 2.2: Polycrystalline graphite mold [DEL83]

Macro- and mesopores (3. in Figure 2.2) originate in the binder between the coke grains because of bubbling during the pyrolysis. The gas produced during pyrolysis escapes from the binder and builds ducts throughout the mold which will become porosities after cooling.

In addition the coke grains get porous by the same mechanism. Micropores are formed mainly between the crystallites parallel to the lattice plane.

The porosity of fine grain graphites is between 15 to 20 % depending on type and amount of binders.

Reactor graphites were used at Research Center Jülich in different research reactors:

FRJ-1 Merlin, FRJ-2 DIDO and AVR.

2.1.1 Research Reactor FRJ-1 Merlin

FRJ-1 was a light-water research reactor of the pool type at Forschungszentrum Jülich with a maximum thermal power of 10 MW. It reached criticality in 1968, was shut down in 1985 and fully dismantled between 1995 and 2009 [FZJ1].

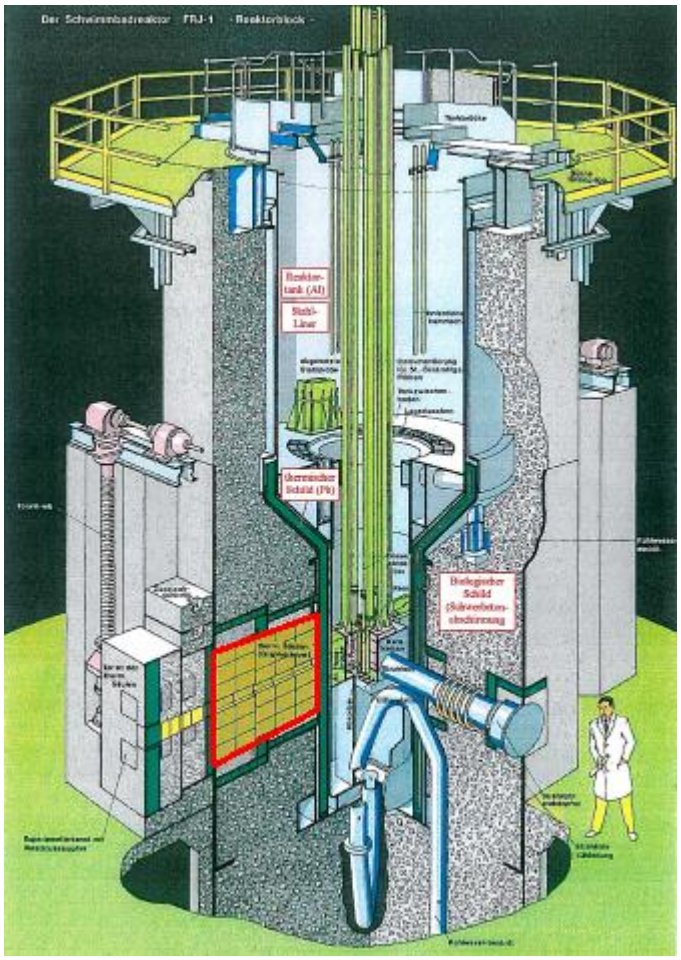

Figure 2.3: Scheme of FRJ-1 Merlin

The nuclear graphite was used in the thermal column (red marks) (see Figure 2.3).

2.1.2 Research reactor FRJ-2 DIDO

FRJ-2 was a heavy water moderated and cooled research reactor with a maximum thermal power of 23 MW. It was the partner reactor of FRJ-1 Merlin but was operated from 1968 till the year 2006. The dismantling of FRJ-2 began in late 2012 [FZJ2] [FZJ3].

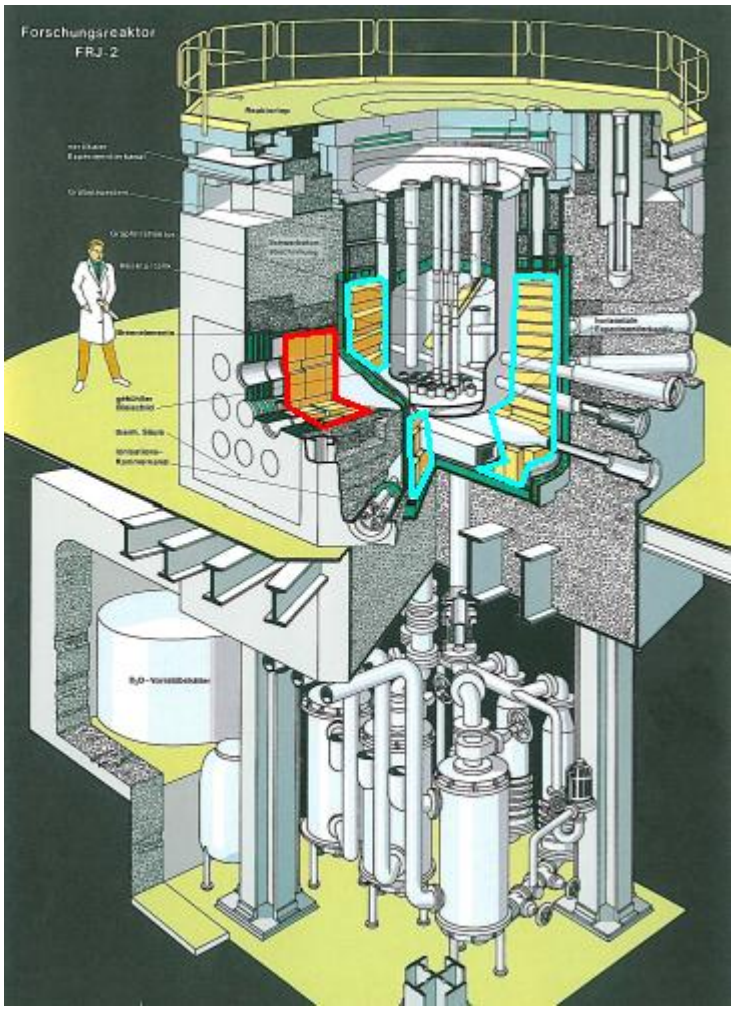

Figure 2.4: Scheme of FRJ-2 DIDO

In this reactor nuclear graphite was used as a reflector (blue marks) and in the thermal column (red marks) (see Figure 2.4).

2.1.3 High-temperature nuclear reactors

Nearly 85 % of all nuclear power plants worldwide are light-water reactors. The high-temperature nuclear reactors were developed because they can have a higher thermodynamic efficiency than light-water reactors [KUG89].

The reactor AVR was used to explore high-temperature reactor designs as realized, e.g. in the THTR-300 where reactor-grade graphite was used to a large extent.

The pebble bed nuclear reactor was developed as a very high temperature reactor of generation IV nuclear reactors. The pebble bed reactors in Germany are AVR in Jülich and THTR-300 in Hamm-Uentrop.

In a pebble bed reactor helium is used as coolant and graphite as construction material, moderator and reflector. Graphite was used because of its capability to absorb a part of the energy of fast neutrons, when they collide with carbon atoms in the graphite lattice.

In addition, the core was surrounded by so called carbon brick, a lower quality graphitic material.

Specific for a pebble bed reactor is the use of spherical coated particles containing nuclear fuel as UO_2 and ThO_2 coated with SiC and pyrocarbon. The diameter of such a sphere is ≈ 6 cm and of the fuel particles is around 0.5 mm.

The core of the reactor is covered with a graphite reflector of 0.5 m width [FIS12].

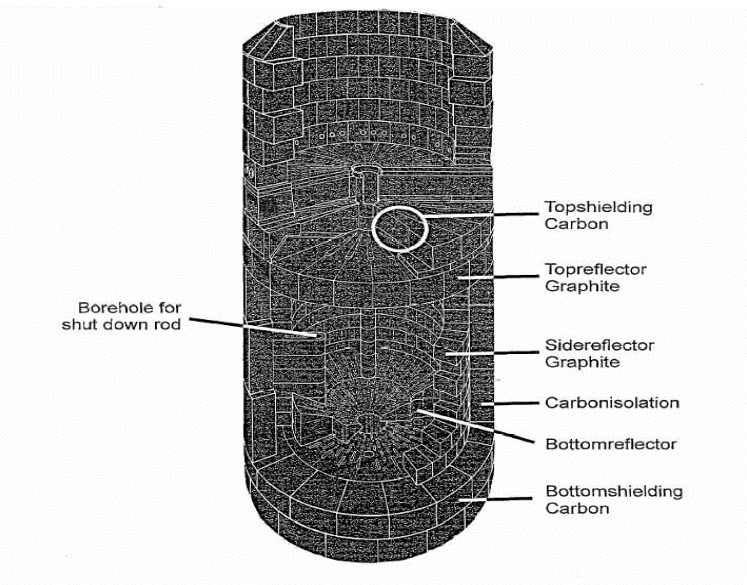

Figure 2.5: AVR graphite and carbon installations [POD04]

2.1.4 Gas –cooled reactors

EDF (Electricite De France) operated in France six gas-cooled reactors, all shutdown now for at least fifteen years. These reactors are of so-called in French, “UNGG” reactor type (Uranium Naturel Graphite Gaz). They were graphite moderated, cooled by carbon dioxide and fuelled with natural metallic uranium.

The Saint-Laurent A2 (SLA2) reactor was commissioned in August 1971. The pressure vessel of this reactor is built of prestressed concrete which also acts as biological shielding. The coolant is CO_2 which circulates from top to bottom at a pressure of 29 bar in the space between the graphite and the Mg-Zr alloy fuel cladding. The operating temperature ranges between 240°C (top) and 470°C (bottom). The thermal power is 1,700 MW. The gross electrical power is 530 MWe and the net electrical power in nominal operation is 515 MWe. The thermal neutron flux (from 10^{-5} eV to 0.5 eV) in the central zone of the core and in the maximum flux plane is 3.12 10^{13} $n.cm^{-2}.s^{-1}$.

It should also be noted that this reactor was shut down between March 1980 and September 1982 following an incident which led to the melting of two fuel elements at the bottom of the F5 M19 C14 channel (loss of cooling of the channel as a result of its obstruction by a metal plate, leading to overheating of the fuel elements).

The SLA2 reactor was finally shutdown on May 25, 1992. It was operated during 11 years full equivalent operating power. It has been defuelled and has been placed in a safe enclosure mode (ventilated by air with a moisture content limited to 50 %) until the final dismantling is performed.

EDF received the authorization to fully dismantle the SLA2 reactor by decree 2012-510 of May 18, 2010. All non nuclear parts of SLA2 nuclear unit have been dismantled (dismantling IAEA level II achieved - figure 2). Up to now, final dismantling (level III) is planned by 2030-2040.

Figure 2: Saint-Laurent A1 (left) and Saint-Laurent A2 (right)

The graphite stack of the SLA2 reactor has the form of a cylinder with a vertical axis 15.73 metres in diameter (13.43 metres of moderator surrounded by a 1.15 m thick reflector) and 10.2 metres high. The total mass of graphite is 2,440 tons including 1,580 tons of moderator and 860 tons of reflector (figure 3).

The stack's network of graphite bricks is a hexagonal mesh with a pitch of 225.16 mm. The elementary graphite blocks are prismatic bars with a hexagonal base whose distance between two opposite faces is equivalent to the network mesh. The side-by-side juxtaposition of 4,429 bars forms a bed, the SLA2 stack consisting of 8 superimposed beds (bed No. 1 is that at the bottom of the stack). Thus, the bars are superimposed and the stack may also be regarded as the juxtaposition of 4,429 columns. The graphite stack comprises:

The lateral reflector consisting only of 828 solid columns surrounding the core;

The moderator (or core) consisting of 3,601 columns: 345 solid columns, 181 bored to 84 mm for the control rods and 3,075 columns bored to 140 mm (basically for the fuel elements).

2.2 Graphite as nuclear waste

During operation reactor graphites are irradiated and acquire radioactive materials. Most activity of graphite molds arises from the neutron induced reactions of carbon, ^{3}H and other activation of stable impurities. The main issue with ^{14}C is its half-life of 5730 years and very high bio-compatibility; therefore it is necessary to keep ^{14}C away from the biosphere, where it could contaminate plants, animals and other life forms. ^{3}H has a half-life of 12.32 years and is also a hazard to the biosphere because of a very quick isotope exchange reaction.

2.2.1 Carbon-14

Carbon - 14 is created in the following nuclear reactions:

- ^{13}C (n, γ) ^{14}C
- ^{14}N (n, p) ^{14}C
- ^{17}O (n, α) ^{14}C

Most of ^{14}C (> 99 %) is formed by the reaction ^{14}N (n, p) ^{14}C.

Nitrogen is an impurity within the graphite mold. Graphite has the ability to adsorb nitrogen onto the boundary layer. Other nitrogen impurities are results of the production process and these impurities normally are embedded in porosities.

2.2.2 Tritium

Tritium (^{3}H / T) is mostly produced by the following nuclear reactions:

- ^{235}U (n, f) ^{3}H
- ^{6}Li (n, α) ^{3}H
- ^{3}He (n, p) ^{3}H
- ^{10}B (n, 2α) ^{3}H
- ^{14}N (n, T) ^{12}C

^{3}H is an isotope of ^{1}H and quickly exchanges with stable hydrogen in a water molecule:

$HT + H_2O \rightarrow HTO + H_2$

This reaction is utilized to trap and analyze the ^{3}H content of the i-graphite.

2.2.3 Other radionuclides

Caesium

Nuclear fission and neutron capture reactions are producing radioactive caesium isotopes ^{134}Cs, ^{135}Cs and ^{137}Cs:

- $^{235}U \rightarrow {}^{137}Cs, {}^{135}Cs$
- $^{235}U \rightarrow {}^{133}Cs\ (n, \gamma)\ {}^{134}Cs$

Impurities of ^{133}Cs can also be a source of ^{134}Cs:

- $^{133}Cs\ (n, \gamma)\ {}^{134}Cs$

The half-lives of these isotopes are:

- ^{134}Cs: 2 years
- ^{135}Cs: 2 E+06 years
- ^{137}Cs: 30.1 years

The sources of these caesium-contaminations are, as mentioned above, both impurities within the nuclear graphite or uranium [POD04].

Europium

The europium isotopes ^{152}Eu, ^{154}Eu and ^{155}Eu are both products of fission reactions and activation of impurities of ^{151}Eu, ^{153}Eu and ^{154}Sm [POD04].

The half-lives of these isotopes are:

- ^{152}Eu: 12.4 years
- ^{154}Eu: 8.5 years
- ^{155}Eu: 4.5 years

Cobalt

The stable ^{59}Co produces ^{60}Co by neutron activation. ^{59}Co is present as an impurity in nuclear graphite [POD04]. ^{60}Co has a half-life of 5.3 years.

2.2.4 Activity inventory

The following tables (Table 2.1, Table 2.2) show that concentration of radioactive materials and amount of activity is significant. Therefore AVR graphite is considered radioactive waste [POD04].

Another problem emerges in the disposal of contaminated graphite materials, because the ^{14}C activity of graphite reflectors would amount to more than 90 % of the total ^{14}C activity licensed for the underground disposal site Konrad in Germany for non-heat-generating radioactive waste [FAC08].

Concentration [ppm]		
Carbon brick	**Reflector**	**Activation product**
30	2	^{3}H
10	2	^{3}H
990,000	1,000,000	^{14}C
4,500	30	^{14}C
15	0.2	^{36}Cl
1,600	30	^{40}K
1,500	100	^{41}Ca
7,000	1,000	^{55}Fe
10	0.2	^{60}Co
40	10	^{63}Ni
2.5	0.05	^{94}Nb
10	2	^{93}Mo, ^{99}Tc
1	0.01	^{134}Cs
100	20	^{133}Ba
2	0.02	^{151}Sm, ^{155}Eu
0.1	0.02	^{152}Eu, ^{154}Eu

Table 2.1: Impurities of AVR graphites [POD04]

Radionuclides	Activity [Bq] Carbon brick	Reflector
^{3}H	6.9 E+15	8.8 E+14
^{14}C	2.9 E+14	4.6 E+12
^{36}Cl	5.9 E+10	1.5 E+09
^{41}Ca	4.5 E+11	5.8 E+10
^{55}Fe	4.0 E+15	1.1 E+15
^{60}Co	1.1 E+15	4.2 E+13
^{63}Ni	8.5 E+12	4.1 E+12
^{93}Mo	4.1 E+08	2.5 E+08
^{99}Tc	3.5 E+07	2.8 E+07
^{134}Cs	3.1 E+13	8.9 E+11
^{133}Ba	7.1 E+11	3.5 E+11
^{151}Sm	1.8 E+10	4.5 E+08
^{152}Eu	2.9 E+07	1.4 E+07
^{154}Eu	3.0 E+11	1.5 E+11
^{155}Eu	2.5 E+12	6.3 E+10
^{166m}Ho	4.3 E+10	2.2 E+09

Table 2.2: Total activity of AVR graphites [POD04] [FIS12]

2.2.5 Disposal of irradiated reactor graphites

In general, the objective of a nuclear waste repository is secure long-term disposal without contact to the biosphere. In Germany, nuclear wastes will be disposed in underground rock formations or salt mines. As many radionuclides have long half-lives ranging from some hundred to millions of years it is necessary to develop a secure repository strategy in order to minimize the transport of radioactive materials to the biosphere. This idea utilizes a multi-barrier system of natural and technical origin, like clay stratums and special containers designed for final repository to seal radionuclides from the biosphere.

Presently, there are four final repositories and final repository projects in Germany:

- Asse repository (existing)
- Morsleben repository (existing)
- Konrad repository (projected)
- Gorleben exploratory mine.

While Gorleben is an exploratory mine and it remains unclear whether radioactive waste will be terminally stored there, Morsleben and Asse already have stores of radioactive waste. The Konrad mine is currently converted into a repository. In compliance with the Atomic Energy Act and current mining legislation, the Federal Office for Radiation Protection (BfS) assumes sole responsibility for operations at the Gorleben and Konrad mines and for the decommissioning of the Morsleben and Asse repositories.

Furthermore, nuclear waste is divided in two categories:

- The first category is heat-generating nuclear waste. Spent nuclear fuel elements and liquid high-level radioactive waste falls into this category.
- The second category is nuclear waste with negligible heat generation. This category contains mostly other primary waste like cleaning cloth, disused tools and plant, used filters or residues from waste water treatment [BfS].

The i-graphite used in nuclear reactors falls into the second category.

The current strategy is a volume-optimized storage in Konrad repository and the irradiated graphite would consume a huge amount of the available space in the repository.

Therefore, separation of ^{14}C from ^{12}C would be a valuable solution to minimize the volume of waste.

2.3 Decontamination procedures for irradiated nuclear graphite

2.3.1 Treatment processes

The decontamination processes for irradiated nuclear graphite are still experimental. The most common idea for a treatment process is the thermal treatment of graphite.

The burning of irradiated graphite would be an efficient method for volume reduction, but is not an option because ^{14}C would be emitted into the atmosphere in form of CO_2.

Therefore pyrolyzing graphite in inert or light oxidizing conditions is better way to separate ^{14}C from ^{12}C [FAC08].

Currently, there are a few thermal treatment processes at Research Center Jülich FZJ.

These processes use a variety of atmospheres, temperature and duration for the graphite treatment.

The atmospheres used for the treatment experiments were:

- inert atmospheres: N_2, Ar
- light oxidizing atmospheres: N_2 + 0.1 % to 1 % O_2, Ar + H_2O

The temperature used range from 750 °C to 1300 °C and the duration of isothermal treatment from 4 to a maximum of 40 hours (see A.2).

Because of these experiments, reforming of graphite with steam is supposed to be a valid way to separate ^{14}C from ^{12}C without a mass loss over 10 %.

2.3.2 Steam reactions with graphite solid bodies

When steam reacts with carbon, carbon monoxide and hydrogen are formed (steam reforming):

$C + H_2O \rightarrow CO + H_2$

The secondary reactions of the steam reforming process are:

$CO + H_2O \rightarrow CO2 + H_2$

$C + 2H_2 \rightarrow CH_4$

$2CO \rightarrow C + CO_2$

Another reaction taking place is the oxidation of CO to CO_2 with the help of CuO:

$CuO + CO \rightarrow CO2 + Cu$

These reactions results in the formation of gaseous CO_2, which can be washed out of the gas flow easily by using the following reaction:

$CO_2 + NaOH \rightarrow Na_2CO_3 + H_2O$

^{14}C is expected predominantly to reside between graphite layers and not bounded within them. Therefore one anticipates extracting a large fraction of ^{14}C by this process.
In order to perform this steam reformation with i-graphites, steam has to reach into the graphite and the CO_2 formed to escape.
Such gas transport mechanisms are typically described as diffusion processes according to Fick's laws:

$$J = \frac{1}{A}\frac{dN}{dt} = -D\frac{\partial c}{\partial x}$$

$$\frac{dc}{dt} = D\frac{\partial^2 c}{\partial x^2}$$

The first law describes the flow, which passes through an area A in a unit of time. The second law describes in a differential equation a time-dependent change of concentration of a gas diffusing in a solid body. The diffusion constant D can also be a unit to measure the speed of the change of concentration.
The porous solid body is subject to different corrosion behaviors depending on temperature as shown in figure 2.6.

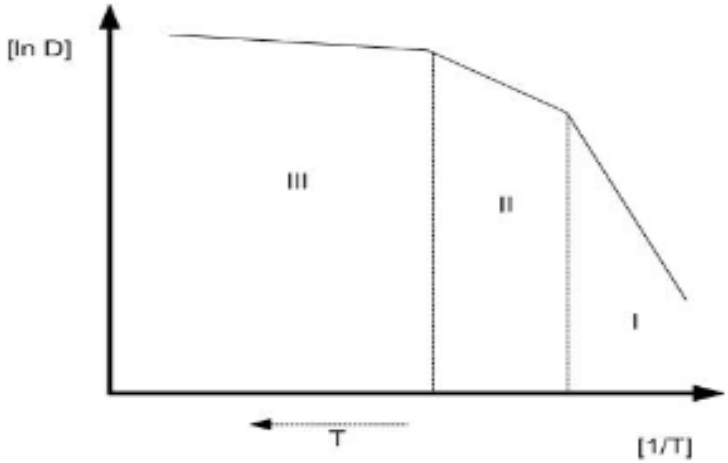

Figure 2.6: Arrhenius diagram of corrosion ranges [FIS12]

Part I has a temperature range of ϑ < 800 °C and is called *chemical range*. The steam diffuses into the porosities and reacts with the whole surface of these porosities (see Figure 2.7). Due to the slow reaction speed there is no change in concentration within the graphite [DEL83].

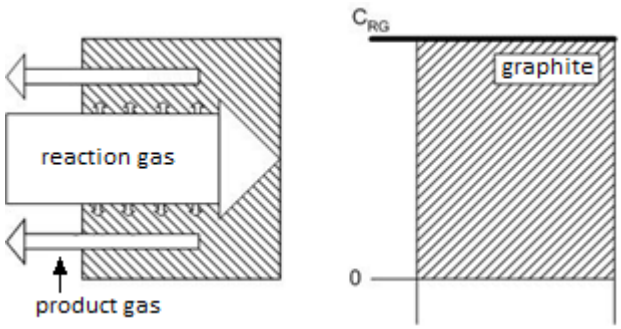

Figure 2.7: Diagram of chemical reaction and concentration trend of reaction gas [FIS12]

Part II has a temperature range of 800 °C < ϑ < 1250 °C and is called *pore diffusion range*. The reaction speed of graphite increases faster than the amount of available steam. Therefore the concentration of steam within graphite decreases with depth; this means the deeper layers stay intact (see Figure 2.8) [DEL83].

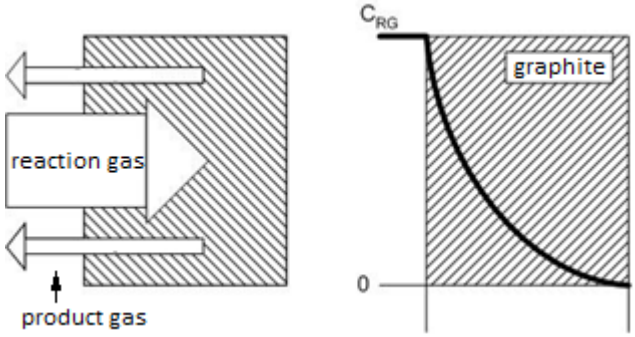

Figure 2.8: Diagram of pore diffusion and concentration trend of reaction gas [FIS12]

Part III has of temperature range of 1250 °C < ϑ < 1400 °C and is called *boundary layer diffusion range*. The steam reacts with the surface of the solid body very fast, so that is not possible for the steam to diffuse into the porosities of the graphite (see Figure 2.9).There is no reaction within the porous solid body, because of the higher temperature. The emerging CO and CO_2, respectively, arise solely from the reaction with the graphite surface [DEL83].

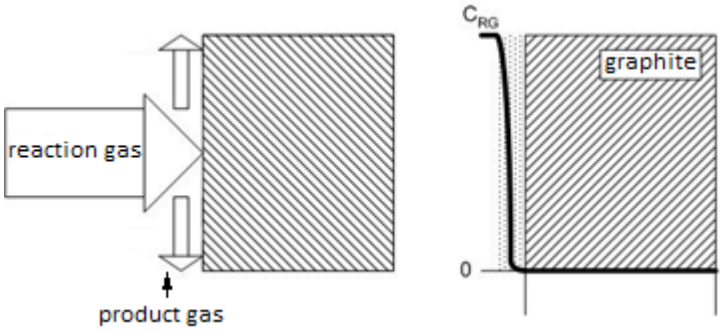

Figure 2.9: Diagram of boundary layer diffusion and concentration trend of reaction gas [FIS12]

The designated reaction of steam and graphite to decontaminate the graphite of ^{14}C and ^{3}H is taking place at temperatures above 900 °C within the pore diffusion range.

2.3.3 Determination of radionuclide release

To determine the release of ^{3}H and ^{14}C the values of the LSC measurement have to be calculated as follows:

$$cpm_{corr.} = cpm - BG$$

$$dpm = \frac{cpm_{corr.}}{\varepsilon}$$

$$A_{mL} = \frac{dpm}{60}$$

$$A_{sample} = A_{ml}\left(V_{db} - (n-1)V_{st}\right)$$

Therefore the final equation is:

$$A_{sample} = \frac{cpm - BG}{60\,\varepsilon}\left(V_{db} - (n-1)V_{st}\right)$$

- A_{mL} is activity in Bq/mL
- A_{sample} is activity in Bq/graphite-sample
- BG is background
- V_{db} is the volume of the full bubbler
- V_{st} is the volume of the taken sample from the bubbler
- ε is the efficiency of LSC measurement derived from tSIE-value
- n is the number of the taken sample

3. Material & Methods

3.1 Steam reforming installation

3.1.1 Equipment

The equipment for steam reforming experiments consists of:

- a high-temperature oven: *Carbolite STF 15/-/180*
- another oven for oxidizing CO to CO2: *Carbolite MTF 10/15/130*
- a humidity generator: *SETARAM WetSys*
- a carrier gas supply system made by *Linde*
- absorbers for ^{3}H and ^{14}C and
- for measuring ^{3}H and ^{14}C: a *Parckard Liquid Scintillation Analyzer TriCarb 2770 TR/SL*

The furnace tube is made of recrystallized alumina (99.7 % Al_2O_3) and has a size of 50 mm × 60 mm × 900 mm (inner diameter × outer diameter × length).

The pipes and junctions are made by *Swagelok*.

The "double bubblers" and the special designed sample holder are made by *Zentralinstitut für Technologie (ZAT)* at Forschungszentrum Jülich.

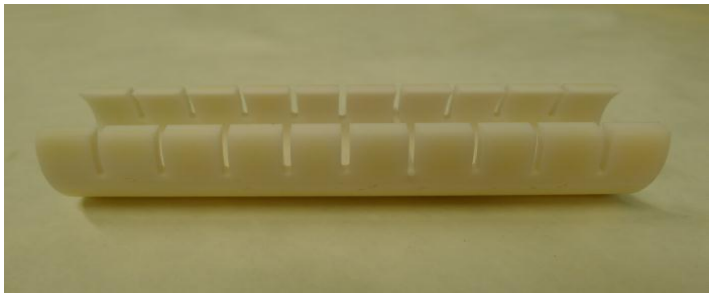

Figure 3.1: A double bubbler and a special designed sample holder made by ZAT

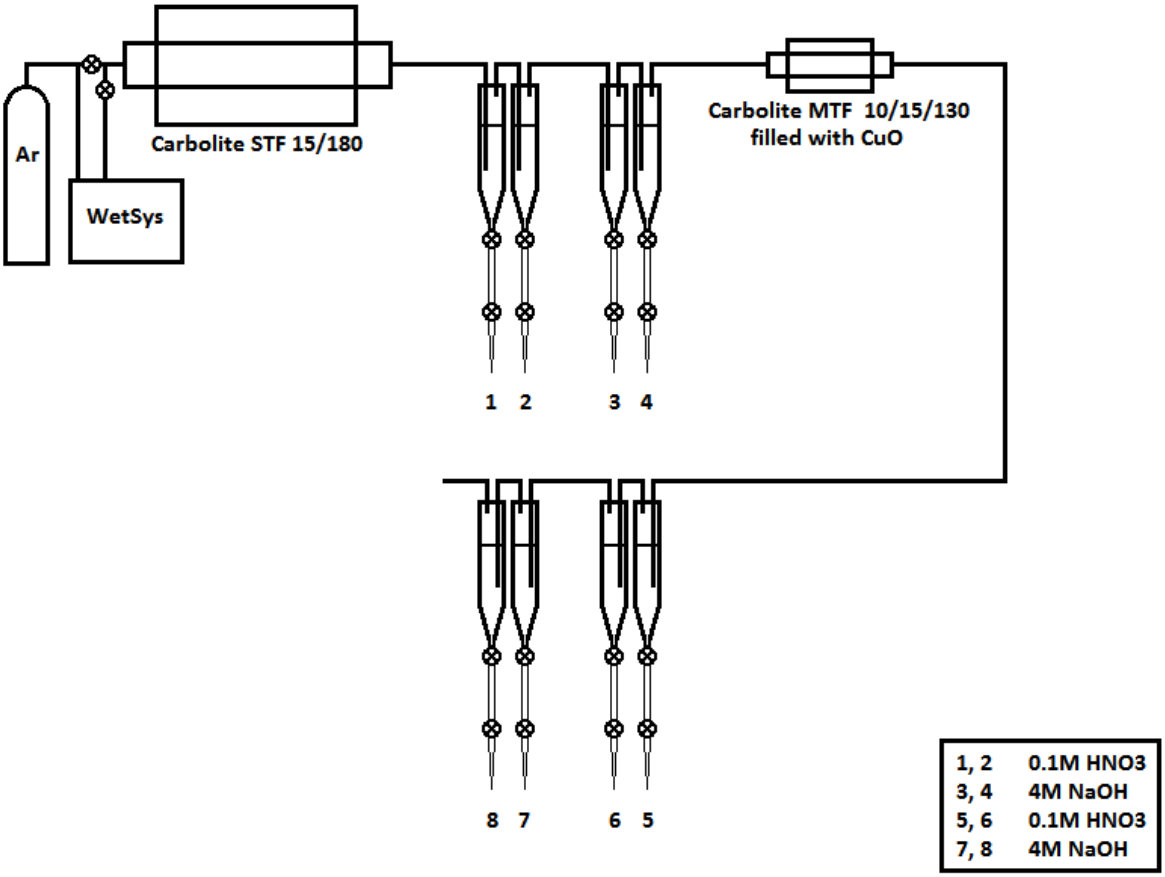

Figure 3.2: A sketch of the treatment installation

3.1.2 Reagents

Following chemicals were used during the experiments:

Sodium hydroxide	NaOH	4 M	*Merck*
Nitric acid	HNO_3	0.1 M	
Copper oxide	CuO		*Merck*
Argon	Ar	> 99.9999 %	*Praxair*
HIONIC FLUOR	LSC Cocktail		*Packard*

3.1.3 Installation description

The experimental installation for graphite decontamination consists of the Carbolite STF 15/-/180 tube furnace with a special aluminum oxide tube and the humidity generator WetSys. At the end of the tube are various “double bubblers” filled with NaOH and HNO_3 and another smaller tube furnace (Carbolite MTF 10/15/130) filled with CuO to enforce the reaction of CO to CO_2.

The WetSys is connected to the argon gas supply line. There is another gas line parallel to the WetSys connected to the furnace in front of the high quality steel flange. Both connections can be activated via gas tap.

The exit of the tube is connected to at least four ”double bubblers”. The first pair is filled with 4 M NaOH to trap redundant tritium (^3H / T) in form of THO. The second pair is filled with 0.1 M HNO_3 to trap redundant $^{14}CO_2$ in form of Na_2CO_3. The smaller tube furnace is placed behind the second double bubblers to ensure that ^{14}CO reacts to $^{14}CO_2$. The third and fourth double bubblers are placed at the exit of the tube furnace and are filled with NaOH and HNO_3 to trap the remaining ^3H and ^{14}C.

All pipes and junctions are made of components made by Swagelok, except the flange adapters which were specially made by ZAT to be compatible with Swagelok components (see Figure 3.2 for installation sketch).

3.2 Materials investigated and sample preparation

3.2.1 DIDO graphite

DIDO graphite samples are not irradiated, so called *virgin*. They have cylindrical shape with a length of 20 mm and a diameter of 8 mm. It was necessary to make a small hack into the samples to minimize the movement on the sample holder.

Before mounting them on the sample holder and inserting them into the furnace tube, the mass of all samples was taken on an analytical balance (*Mettler Toledo XS205 Dualrange*).

Figure 3.3: DIDO graphite sample

3.2.2 Irradiated Merlin graphite

Samples of Merlin graphite were cut in a glove box. They also have nearly cylindrical shape with varying length and diameter. The surface of these samples is much rougher than the DIDO graphite surface.

Before mounting them on the sample holder and inserting them into the furnace tube, the mass of all samples was taken on an analytical balance (*Mettler Toledo XS205 Dualrange*).

Figure 3.4: Merlin graphite samples

The exact specifications of the Merlin samples were:

	Merlin – 1	**Merlin – 2**	**Merlin – 3**
Length [mm]	8 – 10	8 – 11	10 – 12
Diameter [mm]	8	8	8
Weight [g]	0.6472	0.7428	1.0428
Activity of ^{3}H [Bq]	1.12 E+03	1.20 E+03	approx. 1.74 E+03
Activity of ^{14}C [Bq]	2.30 E+02	2.64 E+02	approx. 3.70 E+02

Table 3.1: Merlin graphite samples

3.2.3 Irradiated Saint Laurent Graphite

Samples of Saint Laurent (SLA) graphite were cut in a glove box. They also have nearly cylindrical shape with varying length and diameter.

The SLA samples came each from a different position of the reactor. These positions are set by the level at which the sample were taken.

Before mounting them on the sample holder and inserting them into the furnace tube, the mass of all samples was taken on an analytical balance (*Mettler Toledo XS205 Dualrange*).

The exact specifications of the Saint Laurent A2 samples were:

	SLA R1 1680	**SLA R4 5120**
Length [mm]	18	12.3+/-0.3
Diameter [mm]	8	8
Weight [g]	1.3244	0.93696
Weight after Treatment [g]	1.2958	0.91635
Specific Activity of ^{3}H [Bq/g]	11.9 E+04	12.4 E+4
Specific Activity of ^{14}C [Bq/g]	7.0 E+04	5.9 E+04

Table 3.1: SLA graphite samples

3.3 Treatment and analysis of graphite

3.3.1 Experimental parameters and treatment operations

The experiments were performed with virgin DIDO graphite, irradiated Merlin graphite and irradiated Saint Laurent graphite. As WetSys accepts only input in relative humidity (%), the desired absolute humidity has to be converted. For comparison with other work, e.g. [POD04], also partial pressures are given.

Absolute humidity [g/kg]	Relative humidity [%]	Partial pressure [kPa]
5.0	14.4	0.8
7.5	21.6	1.2
10.0	28.8	1.6
12.5	35.9	2.0
15.0	43.1	2.4
17.5	50.2	2.8

Table 3.2: WetSys parameters

The internal water tank of the WetSys is heated to 35 °C and the supply line to furnace is heated to 40 °C.

For steam reforming it is necessary to eliminate all oxidizing agents besides H_2O. Therefore the tube needs to be flushed with argon before the actual experiment can be started.

3.3.1.1 Virgin DIDO graphite

The experiments with virgin DIDO graphite are used to determine operation conditions of the setup. The use of different temperatures and levels of humidity (Table 3.2) were also necessary to know if the furnace could operate with these parameters.

The operation conditions investigated are:

- Temperatures: 900 °C, 1000 °C, 1300 °C

- Heating rate: 5 K/min
- Gas flow: 5 L/h respectively 85 mL/min
- Time on max. temperature: 2 h

The humidity levels used for virgin DIDO graphite are:

- 900 °C: 14.4 %, 28.8 %, 43.1 %
- 1000 °C: 14.4 %, 21.6 %, 28.8 %, 35.9 %, 43.1 %, 50.2 %
- 1300 °C: 14.4 %, 28.8 %, 43.1 %

The furnace tube needs to be completely flushed with argon before the heating starts; the flushing takes about 1.5 h with a flow of 5 L/h. With the beginning of the heating the gas supply is changed to WetSys.

3.3.1.2 Merlin graphite

Based on the experiments with virgin DIDO graphite, irradiated Merlin graphite is used to determine decontamination factors with a humidity of 10.0 g/kg (1.6 kPa). Three samples were processed with the same parameters.

- Temperature: 1000 °C
- Heating rate: 5 K/min
- Gas flow: approx. 2 L/h (Ar), 25 mL/min (Ar/H_2O)
- Time on max. temperature: 4 h

The humidity level used for Merlin graphite is: 28.8 %.

The furnace is heating up only with argon until it reaches the final temperature of 1000 °C. Then the gas supply line is changed to WetSys to let the furnace operate isothermally with steam. After 4 h of isothermal operation the gas supply line is switched back to argon.

Since it was not possible to determine the end of release with a treatment time of 4 h, a second set of treatment of the samples Merlin-2 and Merlin-3 were performed for a treatment time of 6 h.

In addition when running the second set of experiments with Merlin-3 a mass spectrometer (*InProcessInstruments GAM2000*) was connected to the exhaust line of the tube furnace to gather additional data.

3.3.1.3 Saint Laurent graphite

Based on the experiments with irradiated Merlin graphite, irradiated Saint Laurent (SLA) graphite is used to determine decontamination factors with a humidity of 10.0 g/kg (1.6 kPa). Two samples were processed with the same parameters.

- Temperature: 1000 °C
- Heating rate: 5 K/min
- Gas flow: approx. 2 L/h (Ar), 60 mL/min (Ar/H_2O)
- Time on max. temperature: 10 h

The humidity level used for SLA graphite is: 28.8 %.

Before starting the experiment, the atmosphere was flushed by dry Ar gas and controlled by a mass spectrometer.

Unlike the experiments with Merlin graphite, SLA graphite is heated up from the beginning with steam till 1000 °C. The reason for the change was the mass spectrometer (*InProcess Instruments GAM2000*) that was connected to the exhaust line in order to see the beginning of the water gas reaction and gather further information's about the steam process.

Since the previous experiments showed that longer operation time increases the release of ^{14}C. The heating switched off after 10 h of isothermal operation and the oven cooled down to room temperature.

3.3.2 Liquid scintillation counting

Liquid scintillation counting is a method to determine the activity of beta emitters quantitatively.

The samples need to be dissolved or suspended in a special “scintillation-cocktail” containing an organic solvent and scintillators. Therefore a 1 mL sample of the double bubblers and 1 mL deionized H_2O are mixed with 18 mL *HIONIC FLUOR* LSC cocktail.

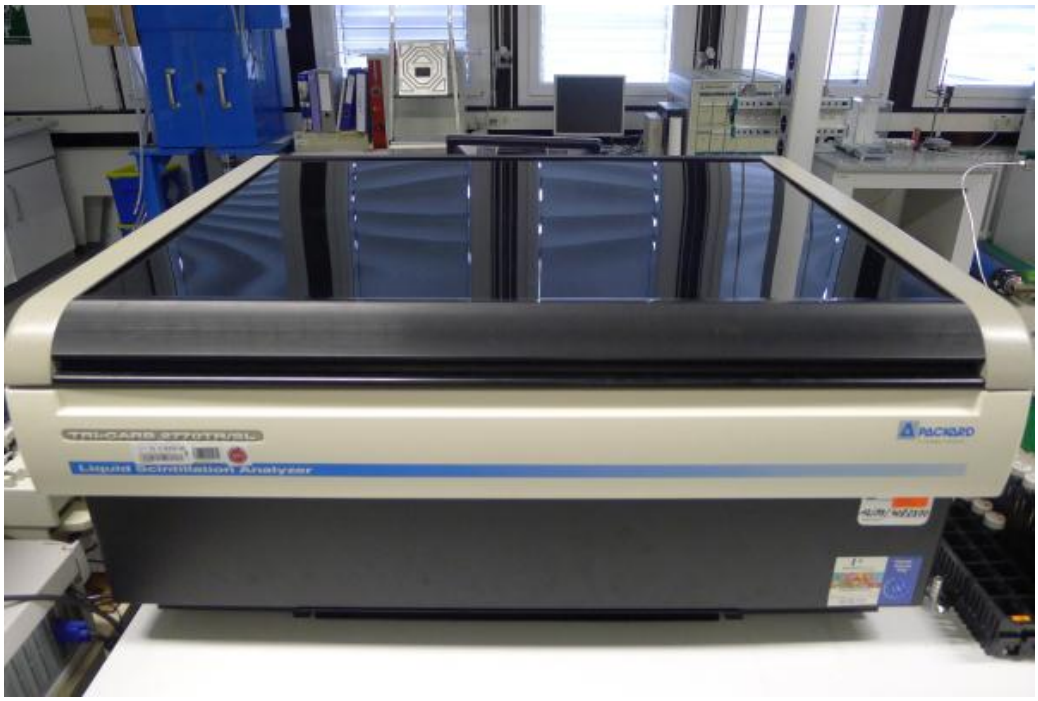

Figure 3.5: Packard Liquid Scintillation Analyzer Tri-Carb 2770 TR/SL

4. Results

4.1 System test

First tests with the tube furnace have shown that it is nearly impermeable to gases, even over long periods of time. This impermeability is important to achieve a closed system. Furthermore the Swagelok stainless steel pipes ensure the impermeability concerning the piping.

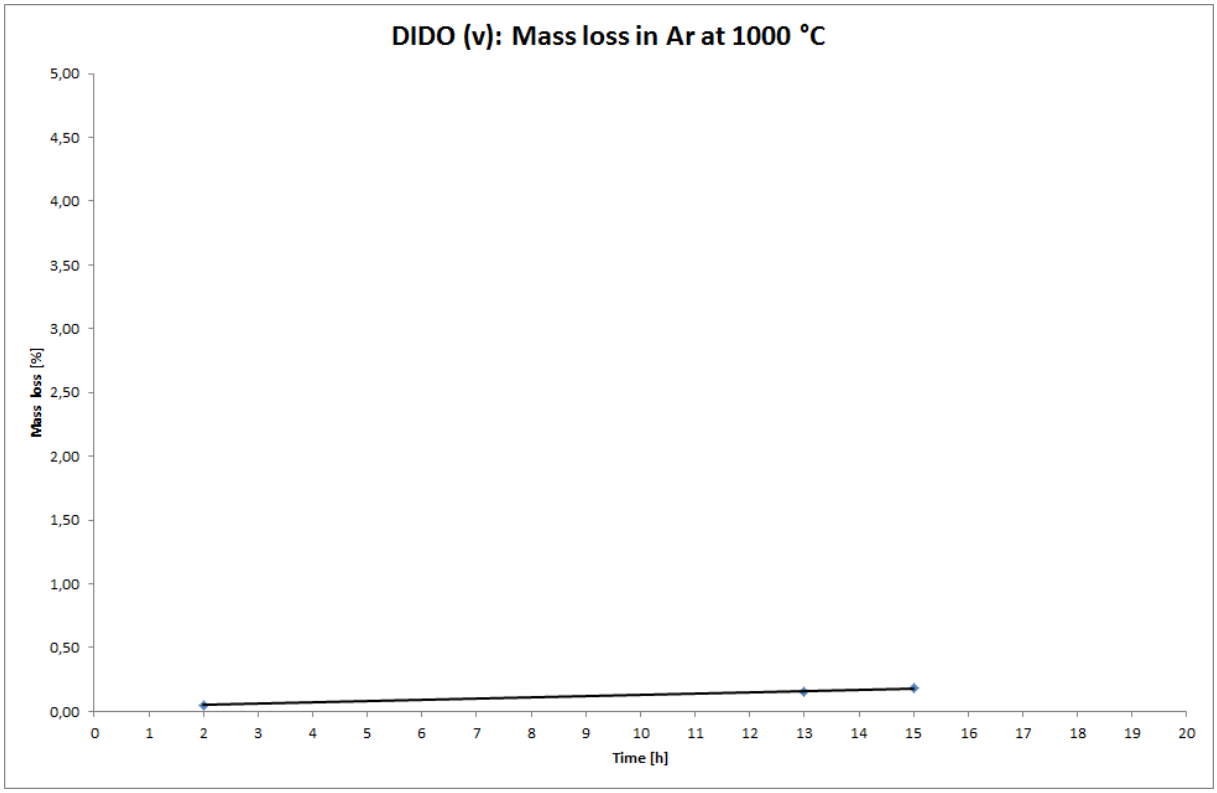

Figure 4.1: Mass loss of DIDO graphite over time

The graph illustrates the very low mass loss over time. The difference in mass loss between 2 h and 15 h of treatment in pure Ar at 1000 °C is just about 0.1 percentage points. This is also indicating that the furnace tube contains the inert atmosphere within.

4.2 Experiments with virgin DIDO graphite

The main task of these experiments was to generate reference data to indicate what parameters should be used with i-graphite. The experiments were all performed with the Carbolite STF 15/-/180 tube furnace, but without bubblers, since there were no radionuclides to trap. As mentioned before (see Chapter 3.3.1), different levels humidity and temperature were used to find suitable operation parameters.

The test series with 900 °C have too low mass losses and with 1300 °C too high mass losses. The test series with 1000 °C have the most suitable mass losses for the desired decontamination.

Furthermore the WetSys parameter of 28.8 % relative humidity, which is 10 g/kg absolute humidity, has served for the tests for irradiated nuclear graphite decontamination.

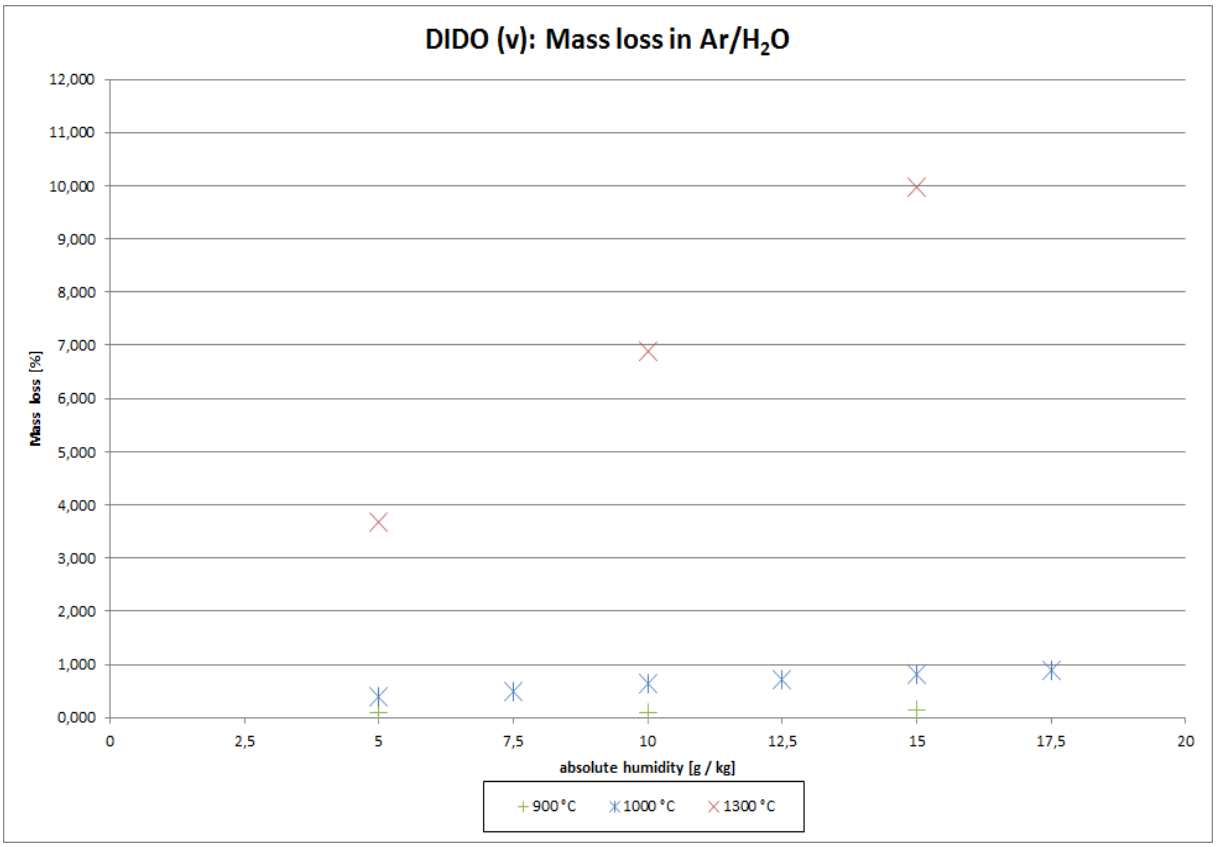

Figure 4.2: Mass loss of DIDO graphite at different temperatures

4.3 Experiments with irradiated Merlin graphite

The thermal treatment experiments with steam as oxidizing agent were performed with Merlin graphite samples described in the previous chapter.

According to previous work of [POD04] it is anticipated that the oxidation rate of ^{12}C is much higher than the release rates of radionuclides, especially ^{14}C and ^{3}H, but the fractional release of these radionuclides is higher than the fractional release of ^{12}C.

4.3.1 Performance of experiments

The first set of steam reforming treatments of Merlin-1 and Merlin-2 were performed without leakage. Regarding Merlin-3 there was a bubbler leakage at the beginning of the experiment, so there is no data for this bubbler.

In the second set of treatment of Merlin-3 there was an uncontrolled gas leakage, which made it impossible to determine the released radionuclides and therefore the original content of radioactivity. The following data of Merlin-3 are estimated.

4.3.2 Release of carbon-14

The release of ^{14}C begins around 600 °C at low rates because of the absence of oxidizing agents. At 1000 °C the oxidizing agent H_2O increases the release of ^{14}C by a great degree. The release of ^{14}C differs in the first treatment steps: the Merlin-1 sample released an amount of 20.1 % ^{14}C after the first treatment, the Merlin-2 sample just released an amount of 11.0 % and Merlin-3 released an amount of 15.0 %.

It could be possible that the Merlin-1 sample had a higher concentration of ^{14}C on the surface or near it, or it was a higher amount of O_2 present in the tube.

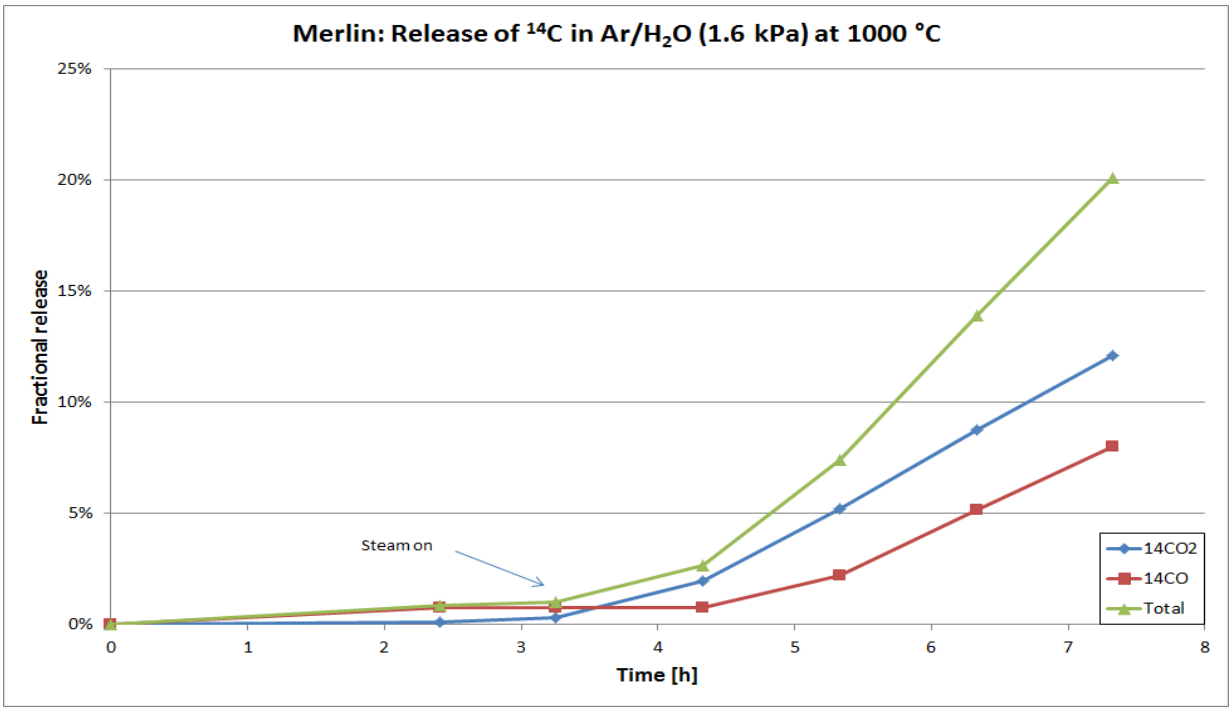

Figure 4.3: Release of ^{14}C of Merlin-1 sample

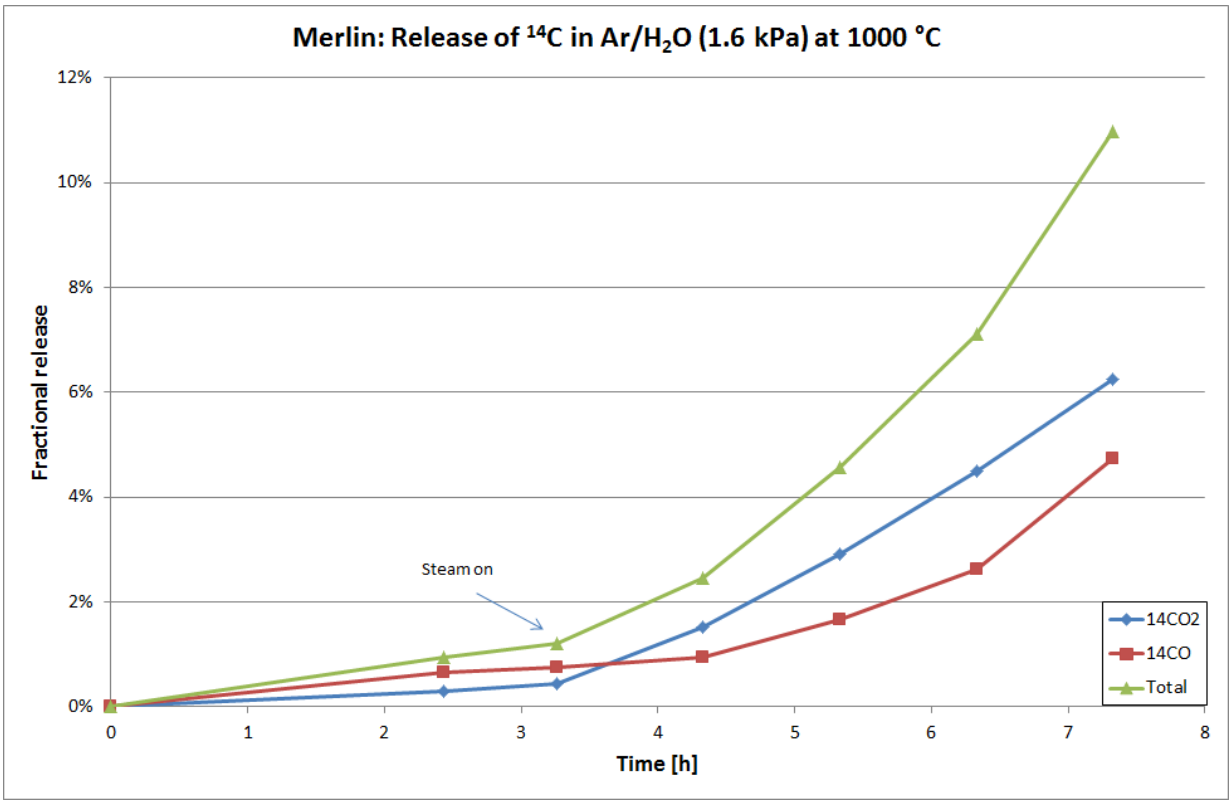

Figure 4.4: Release of ^{14}C of Merlin-2 sample

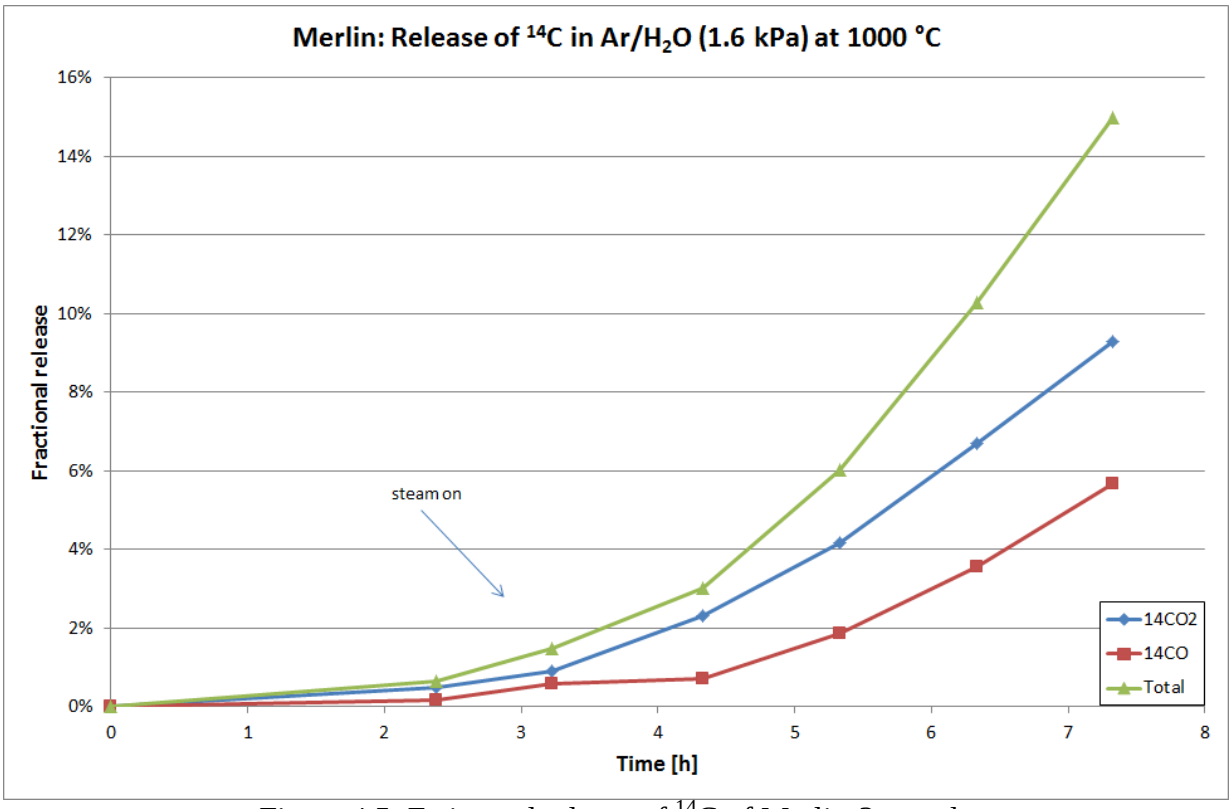

Figure 4.5: Estimated release of ^{14}C of Merlin-3 sample

As mentioned before, it was not possible to determine an end of release of ^{14}C after the first treatment of 4 h. Therefore a second set of treatment performed with Merlin-2 sample and Merlin-3 sample.

The released amount of ^{14}C of Merlin-2 raised to 18.1 % in the second treatment, totaling 29.1 % of release.

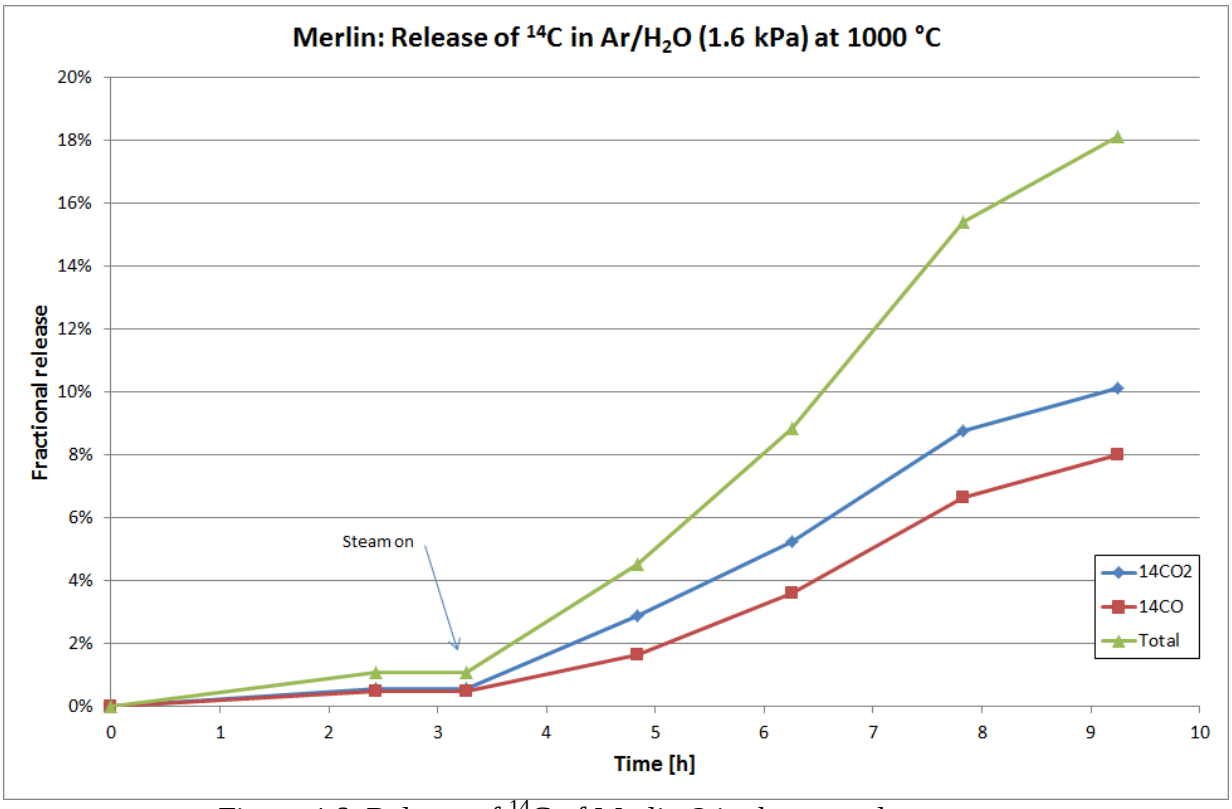

Figure 4.6: Release of ^{14}C of Merlin-2 in the second treatment

The higher release of ^{14}C could be explained with corrosion by the first treatment, creating a better surface for the steam reaction.

4.3.3 Release of tritium

The release rates of tritium do not differ as much as with ^{14}C. In the experiments with Merlin-1 and Merlin-2 the release rates were about 75 %. Merlin-3 had a lower release rate.

Merlin-1 had a release of 73.3 %, Merlin-2 had a release of 77.4 % and Merlin-3 had an estimated release of 65.5 %.

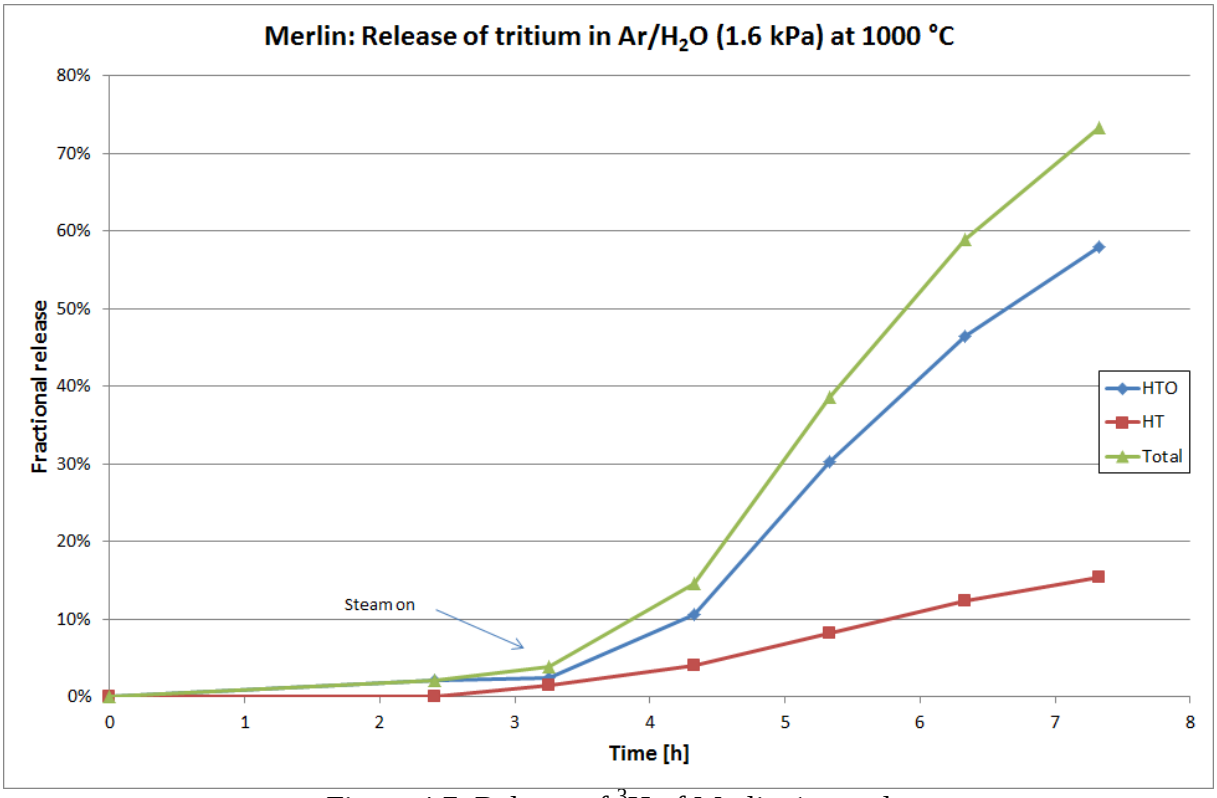

Figure 4.7: Release of ^{3}H of Merlin-1 sample

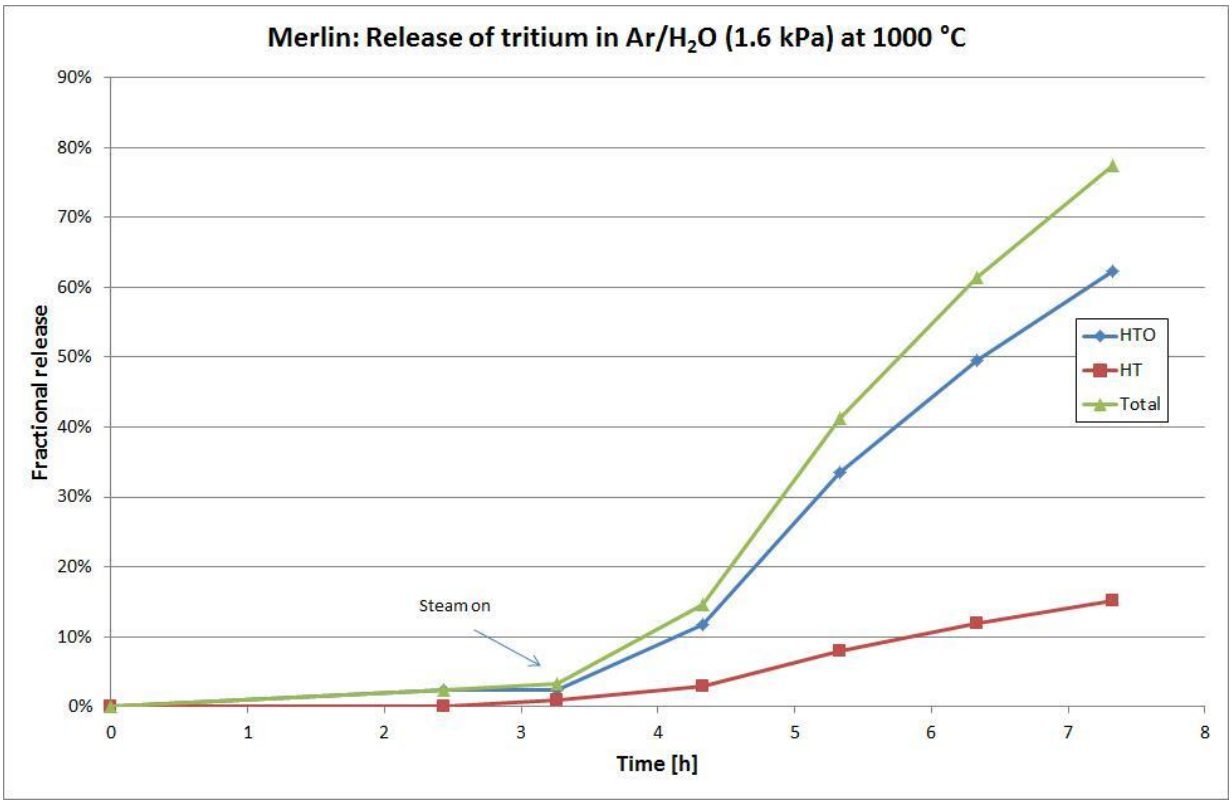

Figure 4.8: Release of ^{3}H of Merlin-2 sample

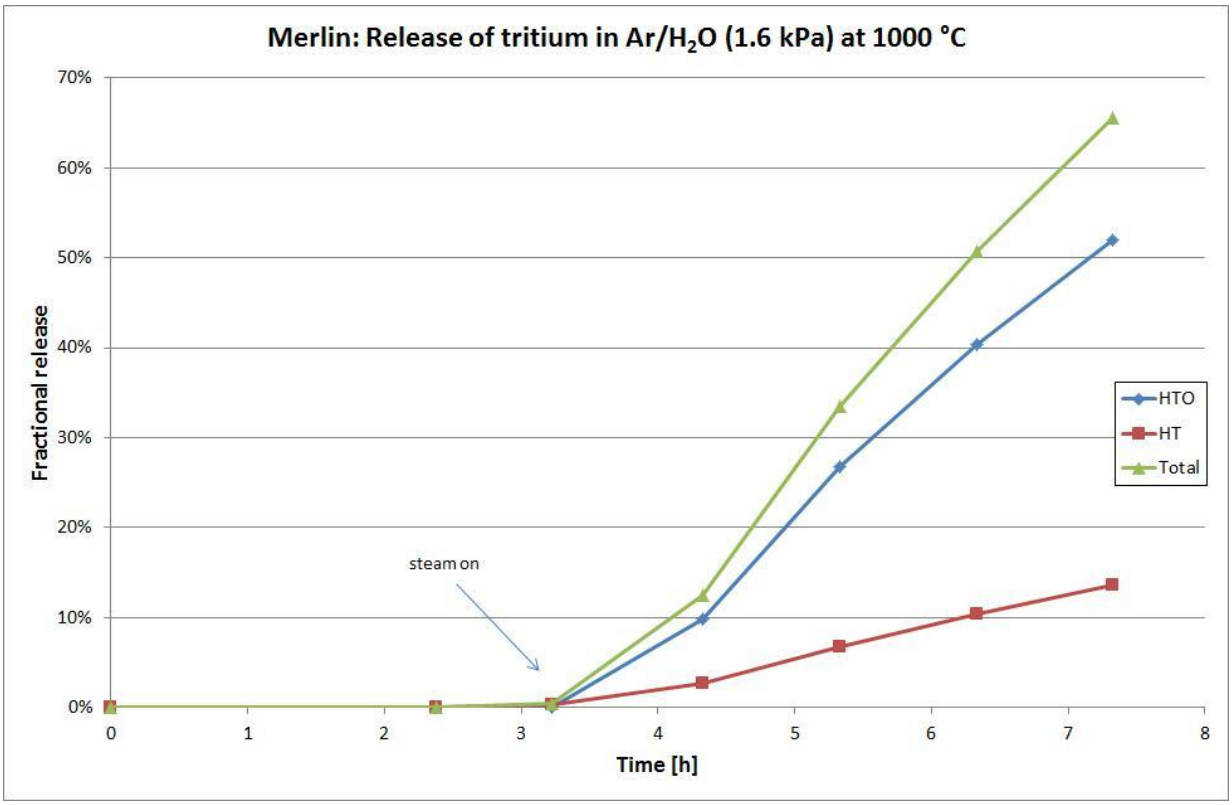

Figure 4.9: Estimated release of ^{3}H of Merlin-3 sample

There is no great difference in the release of ^{3}H, so it can be concluded that most of the release is based on the isotope-exchange and is transferred away as HTO and/or HT with the gas flow. Concerning Merlin-3 the lower release rate could be explained with missing absorbing HNO_3 in one of the bubblers.

Since there is high release rate of ^{3}H the released amount of ^{3}H in the second treatment is much lower - it is around 15 %.

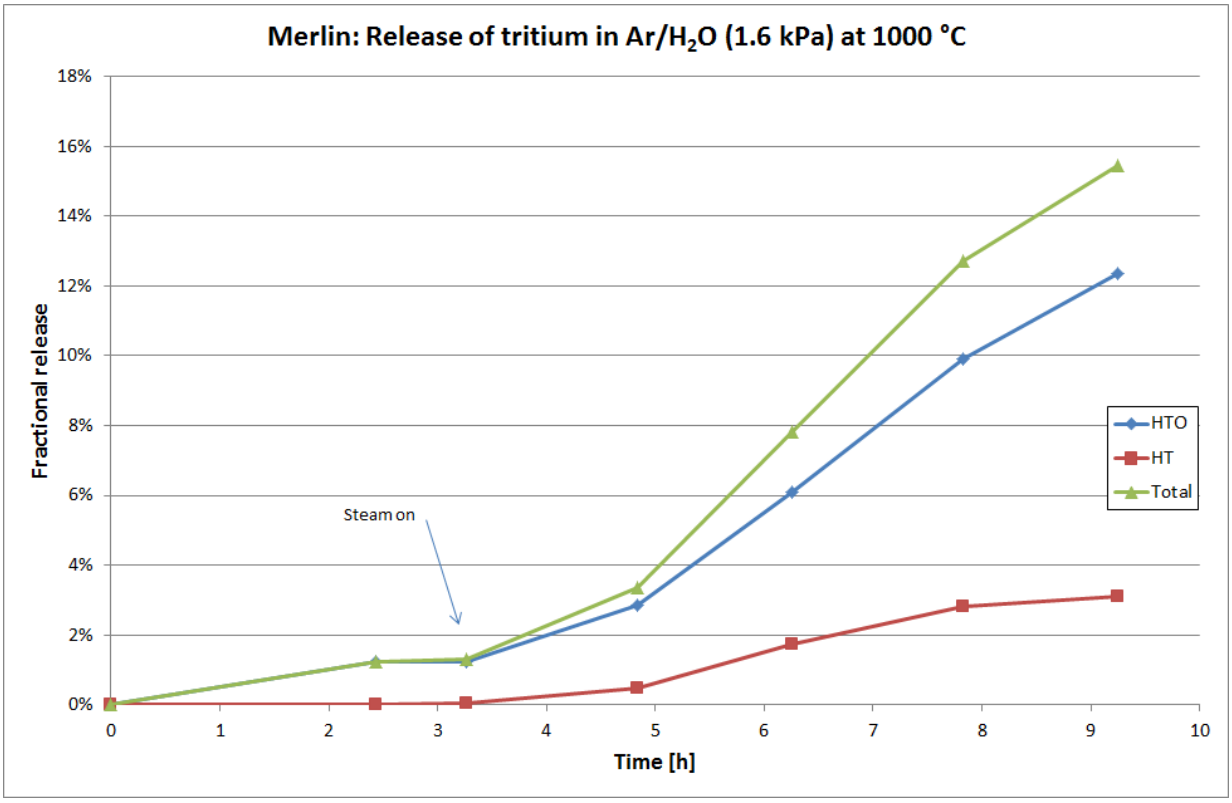

Figure 4.10: Release of ^{3}H of Merlin-2 in the second treatment

4.3.4 Mass spectrometer results

The mass spectrometer has shown that release of radionuclides is taking place even in the heating phase, but it is very low compared to the isothermal treatment phase with WetSys.
One can observe the huge amount of H_2O provided by WetSys within the isothermal phase. As a consequence of that the so called water-gas reaction with graphite is taking place.
Due to the instabilities of the flow the provided water is not stable during the experiment: it is raising. The gaseous emissions of CO and H_2 (see Chapter 2.3.2) are following this trend.
Moreover, an approximately constant emission of CO_2 can be observed, which could be caused by two origins:

- water gas shift reaction
- air ingress during the experiment, leading to the formation of CO_2

In addition one can see that the concentration of H_2 is higher than of CO and CO_2:

- CO_2 (brown line): 410 ± 20 ppm
- CO (red line): 760 ± 20 ppm
- H_2 (violet line): 1200 ± 20 ppm

This can be explained by the water gas shift reaction and the high amounts of water (blue line): a part of the H_2 can come from the water. It was not possible to separate these two effects completely. Therefore, it is likely that an overlapping of these effects was measured (see Figure 4.11).
Successive experiments with the Carbolite STF 15/-/180 (which are not part of this thesis) have revealed an air ingress of up to 15 ppm, but without using WetSys.

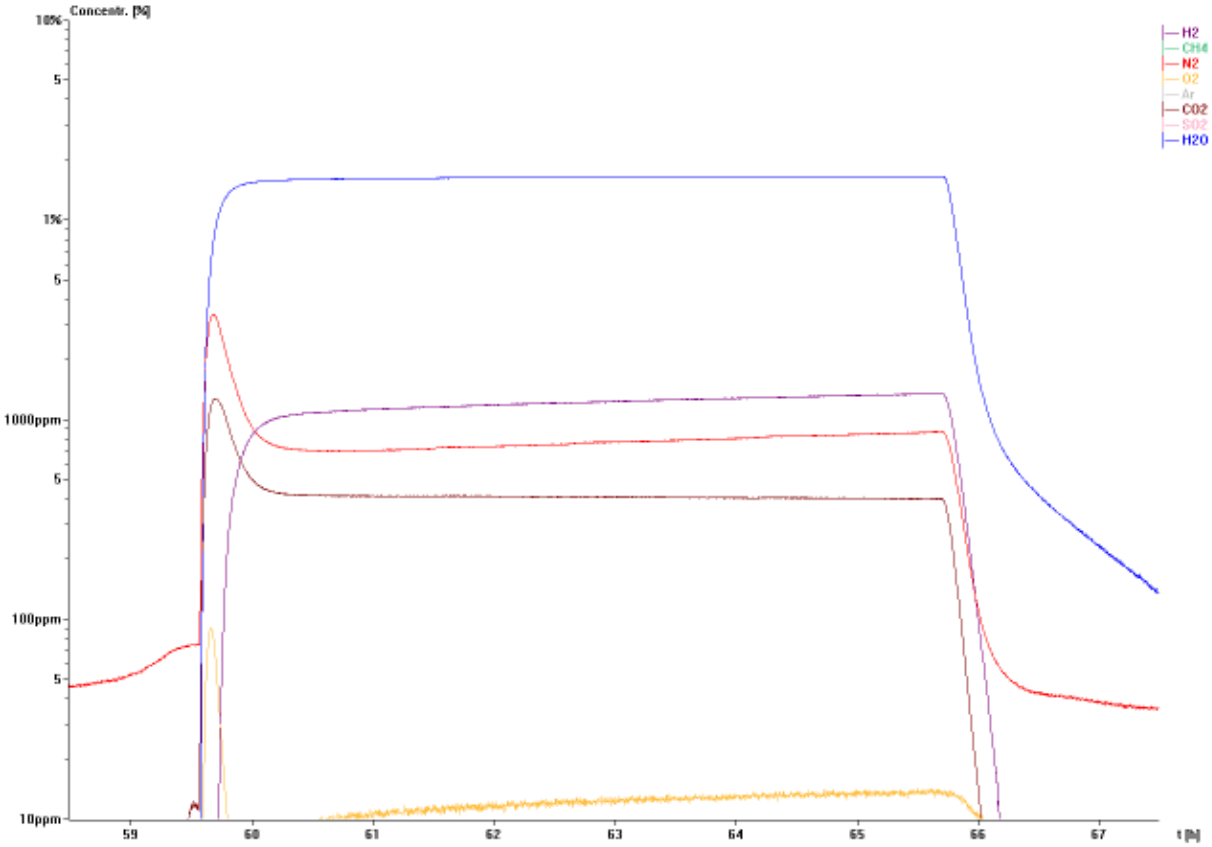

Figure 4.11: Concentration (semi logarithmic) of all gases of Merlin-3, second treatment

4.3.5 Determination of decontamination factors

The decontamination factor is a measure of the effectiveness of a decontamination process. It is the ratio of the original contamination to the remaining radiation after decontamination. A value of 1000 and above is excellent; 10 and below is poor [HUT].

The decontamination factors (DF) are determined with the following formula:

$$DF = \frac{A_{untreated}}{A_{treated}}$$

The activities $A_{untreated}$ and $A_{treated}$ are measured separately for ^{14}C and ^{3}H in Bq/g.

- $A_{treated}$ is the rest activity measured with LSC after combusting the treated sample in O_2
- $A_{untreated}$ is the sum of the rest activity and the activity released in the treatments

Subtracting the background is not necessary because this was already done in a previous calculation step.

Sample	Treatment gas	ϑ [°C]	Treatment time [h]	
			Heating	Isothermal
Merlin-1	Ar + H_2O (1.6 kPa)	1000	3:15	4
Merlin-2	Ar + H_2O (1.6 kPa)	1000	3:15	10
Merlin-3	Ar + H_2O (1.6 kPa)	1000	3:15	10

Table 4.1: Experimental conditions

Sample	Before treatment		After treatment	
	A(^{3}H) [Bq/g]	A(^{14}C) [Bq/g]	A(^{3}H) [Bq/g]	A(^{14}C) [Bq/g]
Merlin-1	1.73 E+03	3.55 E+02	4.70 E+02	2.88 E+02
Merlin-2	1.62 E+03	3.56 E+02	1.20 E+02	2.62 E+02
Merlin-3	≈ 1.67 E+03	≈ 3.55 E+02	7.49 E+01	1.61 E+02

Table 4.2: Activity before and after steam reforming

Sample	Mass loss [%]	Release [%]					
		HTO	HT	^{3}H total	$^{14}CO_2$	^{14}CO	^{14}C total
Merlin-1	1.58	58.0	15.4	73.4	12.1	8.0	20.1
Merlin-2	3.66	74.4	18.2	92.9	16.3	12.7	29.0
Merlin-3 (after 4h)	1.48	≈ 51.9	≈ 13.6	≈ 65.5	≈ 9.3	≈ 5.7	≈ 15.0

Table 4.3: Mass loss and release of ^{3}H and ^{14}C

Sample	Decontamination factor	
	^{3}H	^{14}C
Merlin-1	3.7	1.2
Merlin-2	13.4	1.4
Merlin-3	≈ 22.3	≈ 2.2

Table 4.4: Decontamination factors of ^{3}H and ^{14}C

4.4 Experiments with irradiated Saint Laurent graphite

The thermal treatment experiment with steam as oxidizing agent was done with Saint Laurent graphite samples. It was prepared and settings were arranged like described in the previous chapters, adjusted by a few exceptions for the mass spectrometer.

4.4.1 Performance of experiments

While the experiment was running, it was observed by a mass spectrometer. This was done to determine the compounds of the atmosphere inside the oven. To ensure that no water was condensate out in the oven or piping, the oven was heated up to 200 °C where the mass spectrometer was set a baseline.

While the oven was flushed by Argon gas the composition of gases inside the oven were constantly changing to a certain point at which no O_2 or N_2 was detectible. Assuming that those gases are the first detectable gases provided by leakages, the oven was considered leakage free.

The gas flow was set higher than in the previous experiments because of the mass spectrometer that needs a gas flow of at least 60 mL/min for a correct measurement.

4.4.2 Release of carbon-14

The release of ^{14}C begins around 600 °C at low rates like the water gas reaction predict. From that point the oxidizing agent H_2O benefits the release of ^{14}C. The release of ^{14}C is nearly linear after the starting phase and differs after treatment between the probed samples a little: SLA2 R1 sample released an amount of 6.9% and the SLA2 R4 sample just released an amount of 8.2%.

After 12 hours and 40 minutes the oven is cooling down again. At this moment the linearity stops and the released amount of ^{14}C is decreasing.

Again it was not possible to determine an end of release of ^{14}C after 10 hours of treatment.

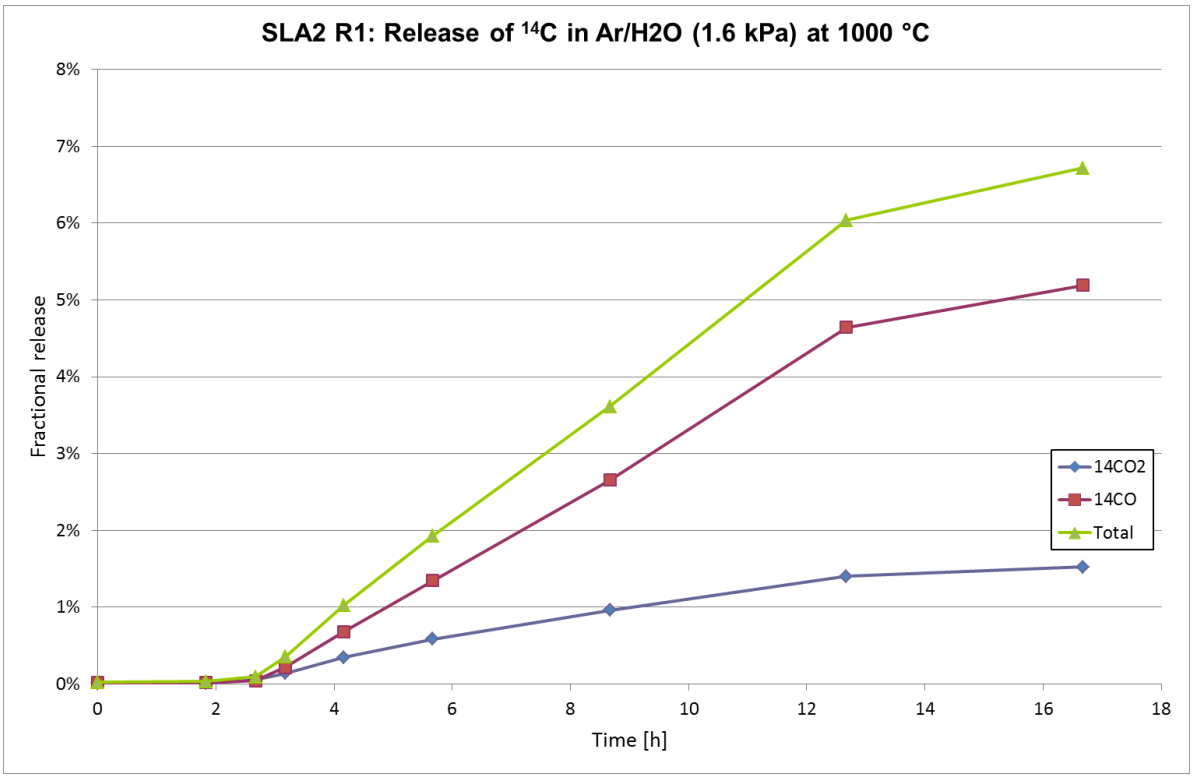

Figure 4.12: Release of ^{14}C of SLA2 R1 sample

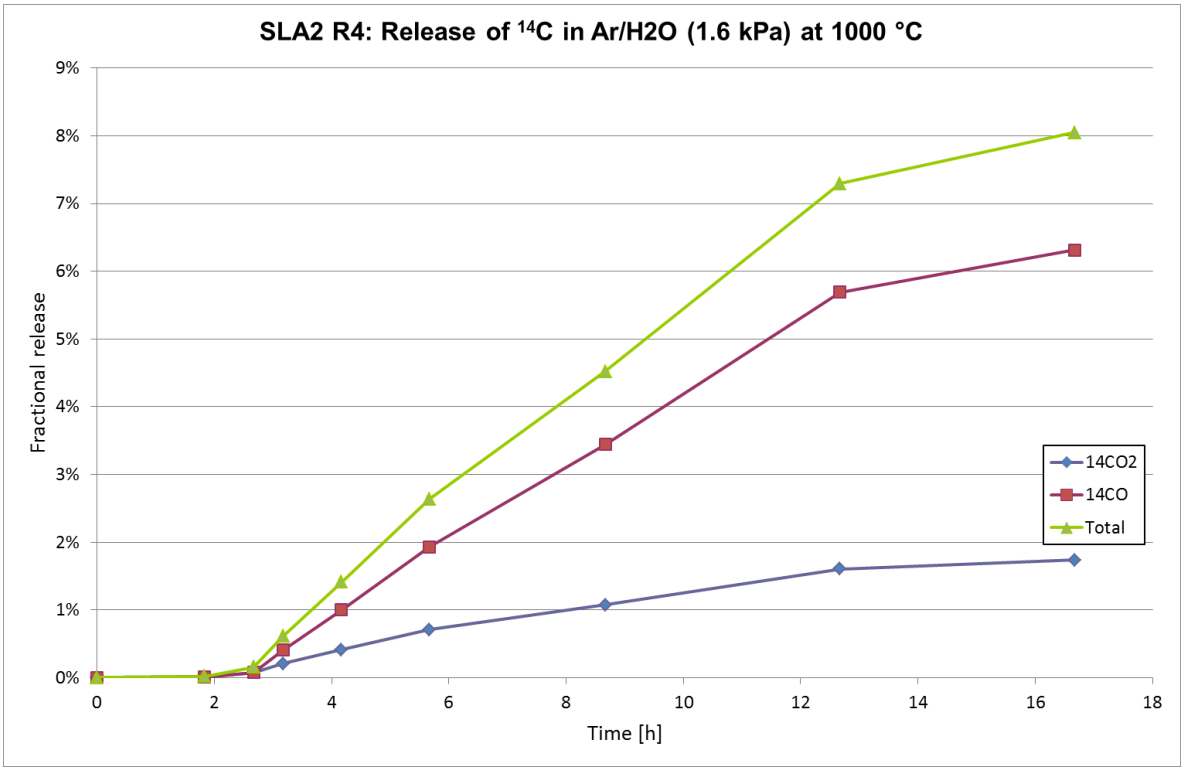

Figure 4.13: Release of ^{14}C of SLA2 R4 sample

4.4.3 Release of tritium

The release rates of tritium do differ around the same percentage amount as with ^{14}C. SLA2 R1 had a release of 39.7 % and SLA2 R4 had a release of 50.3 %. The release of tritium starts at the same time as ^{14}C is beginning to release. But in difference to ^{14}C it is not linear instead it raises high in the beginning and decreases over time.

After switching the heating of the oven off the tritium release is further decreasing. Nevertheless it was not possible to determine an end of release of tritium after 10 hours of treatment.

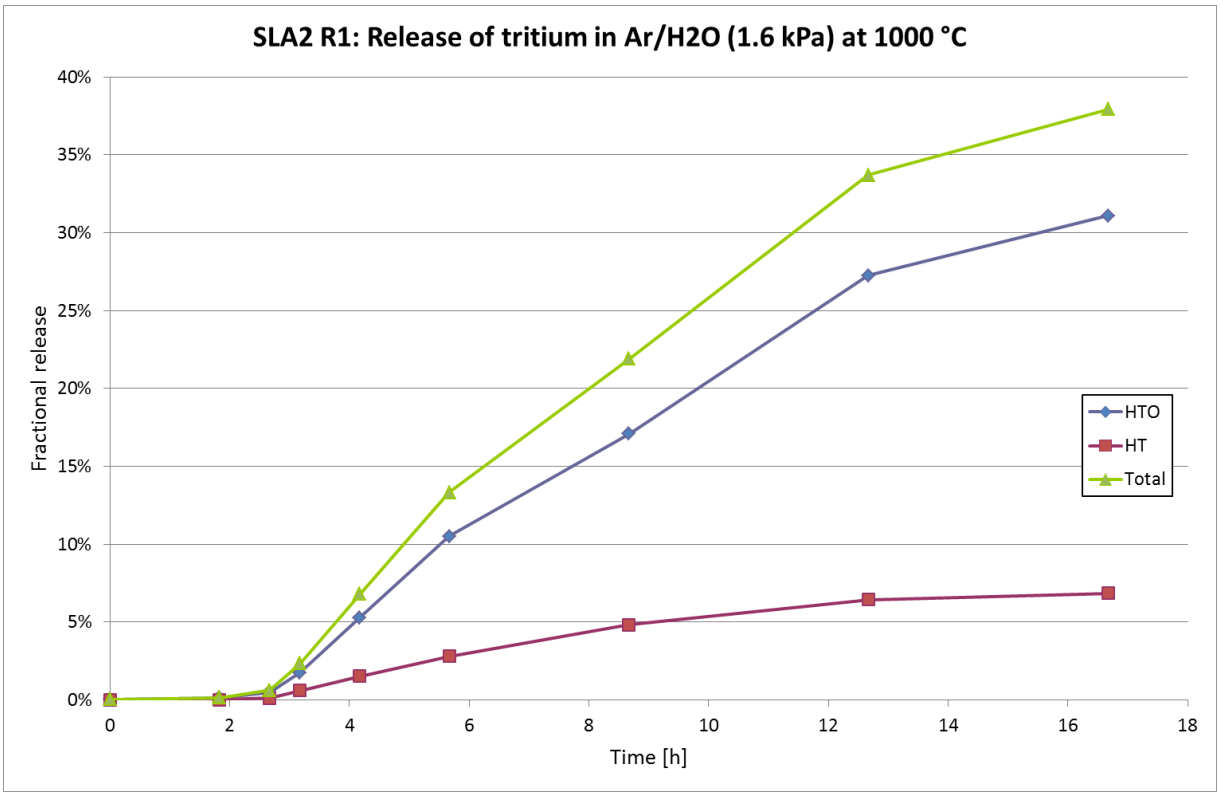

Figure 4.14: Release of tritium, SLA2 R1 sample

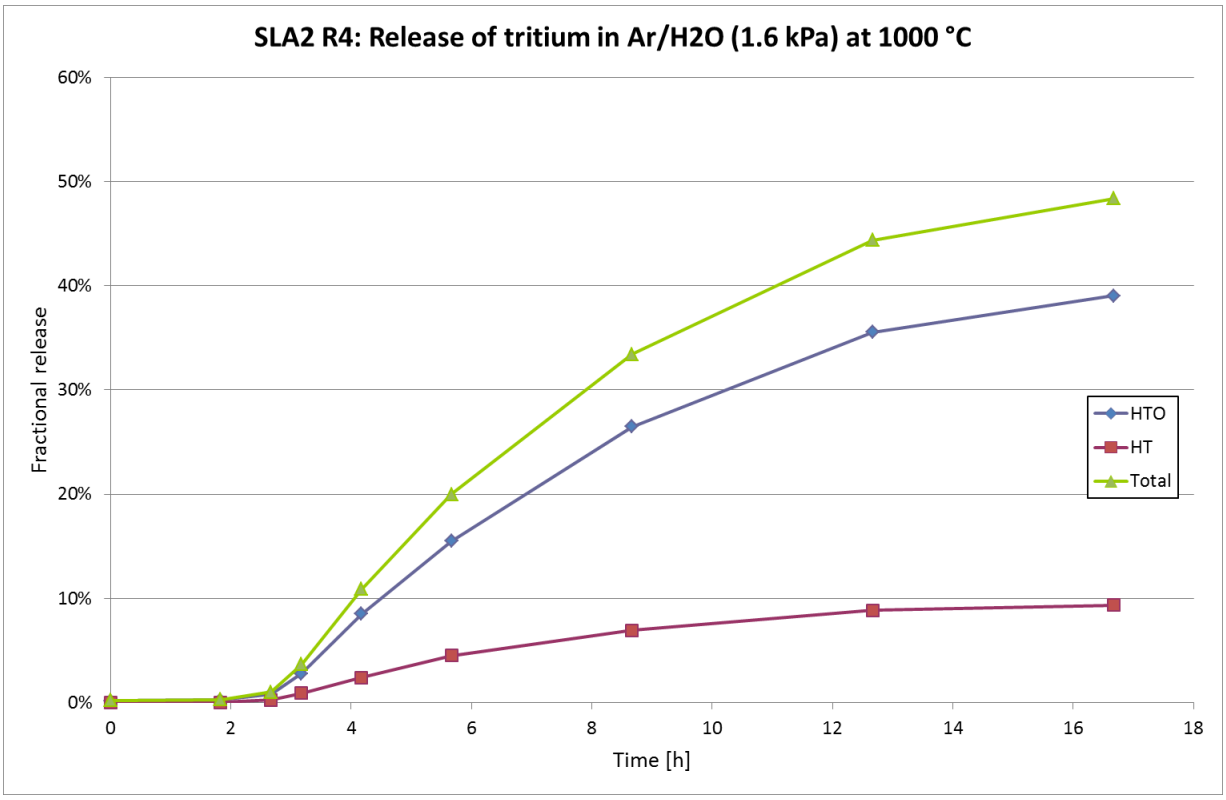

Figure 4.15: Release of tritium, SLA2 R4 sample

4.4.4 Determination of decontamination factors

The decontamination factor is a measure of the effectiveness of a decontamination process. It is the ratio of the original contamination to the remaining radiation after decontamination. A value of 1000 and above is excellent; 10 and below is poor [HUT].

The decontamination factors (DF) are determined with the following formula:

$$DF = \frac{A_{untreated}}{A_{treated}}$$

The activities $A_{untreated}$ and $A_{treated}$ are measured separately for ^{14}C and ^{3}H in Bq/g.

- $A_{treated}$ is the rest activity measured with LSC after combusting the treated sample in O_2
- $A_{untreated}$ is the sum of the rest activity and the activity released in the treatments

Subtracting the background is not necessary because this was already done in a previous calculation step.

Sample	Treatment gas	ϑ [°C]	Treatment time [h]	
			Heating	Isothermal
SLA2-R1	Ar + H_2O (1.6 kPa)	1000	2.66	10
SLA2-R4	Ar + H_2O (1.6 kPa)	1000	2.66	10

Table 4.5: Experimental conditions of SLA2

Sample	Before treatment		After treatment	
	A(^{3}H) [Bq/g]	A(^{14}C) [Bq/g]	A(^{3}H) [Bq/g]	A(^{14}C) [Bq/g]
SLA2-R1	1.19 E+05	6.98 E+04	8.31 E+04	4.04 E+04
SLA2-R4	1.24 E+05	5.92 E+04	5.45 E+04	5.48 E+04

Table 4.6: Activity before and after steam reforming of SLA2

Sample	Mass loss [%]	Release [%]					
		HTO	HT	^{3}H total	$^{14}CO_2$	^{14}CO	^{14}C total
SLA2-R1	2.16	26.3	5.7	32	1.2	3.9	5.1
SLA2-R4	2.20	46.0	10.9	56.9	2.1	7.3	9.4

Table 4.7: Mass loss and release of ^{3}H and ^{14}C of SLA2

Sample	Decontamination factor	
	^{3}H	^{14}C
SLA2-R1	1.44	1.03
SLA2-R4	2.27	1.08

Table 4.8: Decontamination factors of ^{3}H and ^{14}C of SLA2

5.0 Results obtained by other Carbowaste Partners

Steam Treatment of i-graphite has been performed also by EDF and Moscow Scientific and Industrial Association "Radon". In this chapter the experimental results of the partners will be firstly presented, together with the available information on the boundary conditions applied; in a second instance the comparison of results, discussion and common interpretation will be dealt.

5.1 Steam Reforming applied in EDF

Similarly to what has been done in FZJ, EDF performed several investigations on virgin and irradiated graphite (SLA2) in order to better comprehend the applicability of the steam reforming as an efficient decontamination process. Several pre-experiments with virgin graphite were performed, aimed to quantify the gasification rates at different temperature and gas mixtures: the obtained results are reported in Table 5.1.1. In all cases, the rate of mass loss showed, as expected, an increasing trend with the temperature. However, with a 100% steam flow (further details on the steam conditions are not available) the rate of mass loss showed to be much lower – from 2 to 5 times – than the ones in the case of Steam/Oxygen 60/40 flow, with the same treatment applied temperature. Following these results, temperatures allowing the gasification of graphite at reasonable rates are starting from 1100 °C for pure steam reforming, while temperatures higher than 900 °C for steam/oxygen 60/40 flow have to be considered.

Temp	Gas Flow	Steam	Oxygen	Mass Loss Rate	Mass Loss
°C	Cc/min	%	%	g/hr	%
900	300	100	0	0.16	5
1100	300	100	0	1.13	23
900	300	60	40	0.83	25
1100	300	60	40	1.35	46

Table 5.1.1: Preliminary tests performed at EDF to determine the reaction rates and the overall mass loss in various conditions. Note: Each sample contained 20 g i-graphite processed for 6 hours.

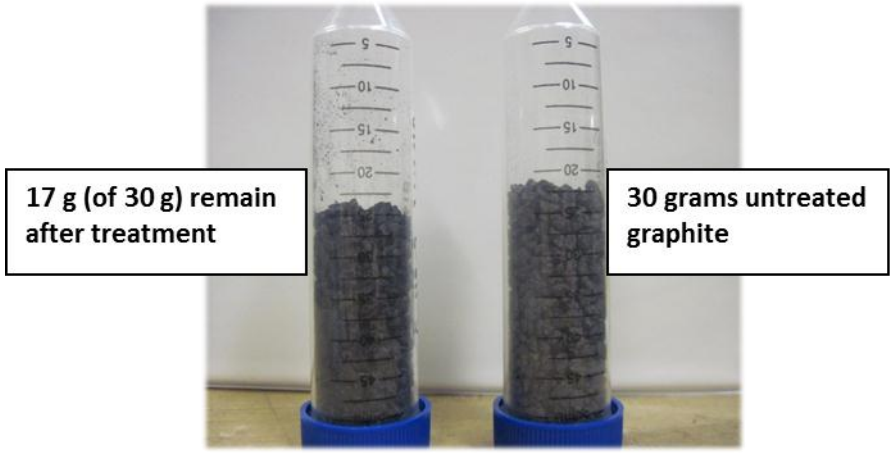

Figure 5.1.1: Visual inspection of crushed graphite samples, before and after treatment

Figure 5.1.1 provides a visual overview of the corrosion effect that is taking place, in general, with graphite: even in front of a 45% mass loss due to steam gasification, the volume of the graphite is reduced only of about 20%. This fact underlines the regime of corrosion that is taking place, typical for porous materials, strongly bound to temperature and reaction gases.

The experimental equipment is shown in Fig. 5.1.2. The main elements are:

- Steam Reformer
- Condenser
- Thermal Oxidizer
- Washing bottles with basic solution

Typical process conditions are the followings:

- Roasting Temperature: 1300°C
- Graphite Sample Size: 15-20 g
- Gas Flow: 60-300 cc/min
- Thermal Oxidizer Temperature: 1000°C
- Bubbler Trapping Solution: NaOH (4M)
- Roasting Times: Up to 20 hours

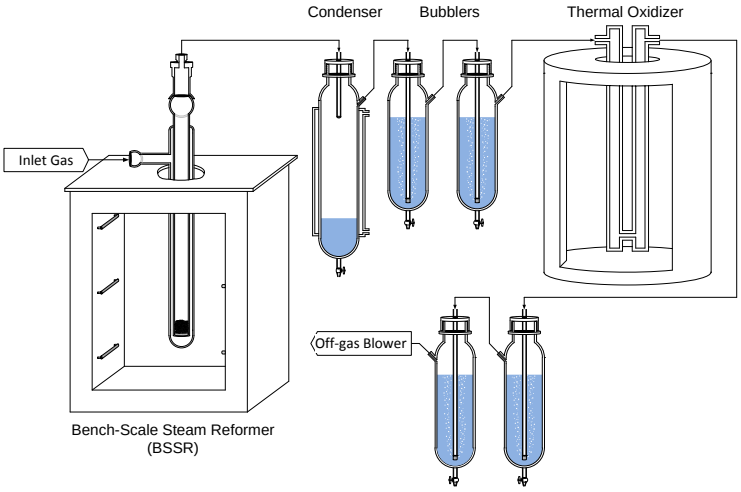

Figure 5.1.2: Scheme of the experimental setup in EDF for steam reforming of i-graphite – bench scale

Experiments with i-graphite (SLA2) were performed with the aim of releasing the highest amount of C-14, H-3 and Cl-36 in conjunction with a low mass loss. The goal for a decontamination process has been estimated around 5% maximum mass loss, in the way to obtain a concentrated and selective separation of volatile radionuclides from the bulk graphite. Tests with i-graphite were performed under the following conditions: 15 g sample/test roasting at 1300°C with 60 cc/min flow; samples soaked in water for 4 weeks. Samples F-1 & F-2 roasted for 17 hours; samples F-3 & F-4 roasted one day for 8 hours and the following day for 6 hours. The operational choices focused on the selection of the treatment gas mixture:

- Low Hydrogen content (unknown), 10% steam (reference temperature not available)
- Low Hydrogen content (unknown), 5% steam (reference temperature not available)
- Double Hydrogen content (unknown), 10% steam (reference temperature not available)

The results are summarized in Fig. 5.1.3.

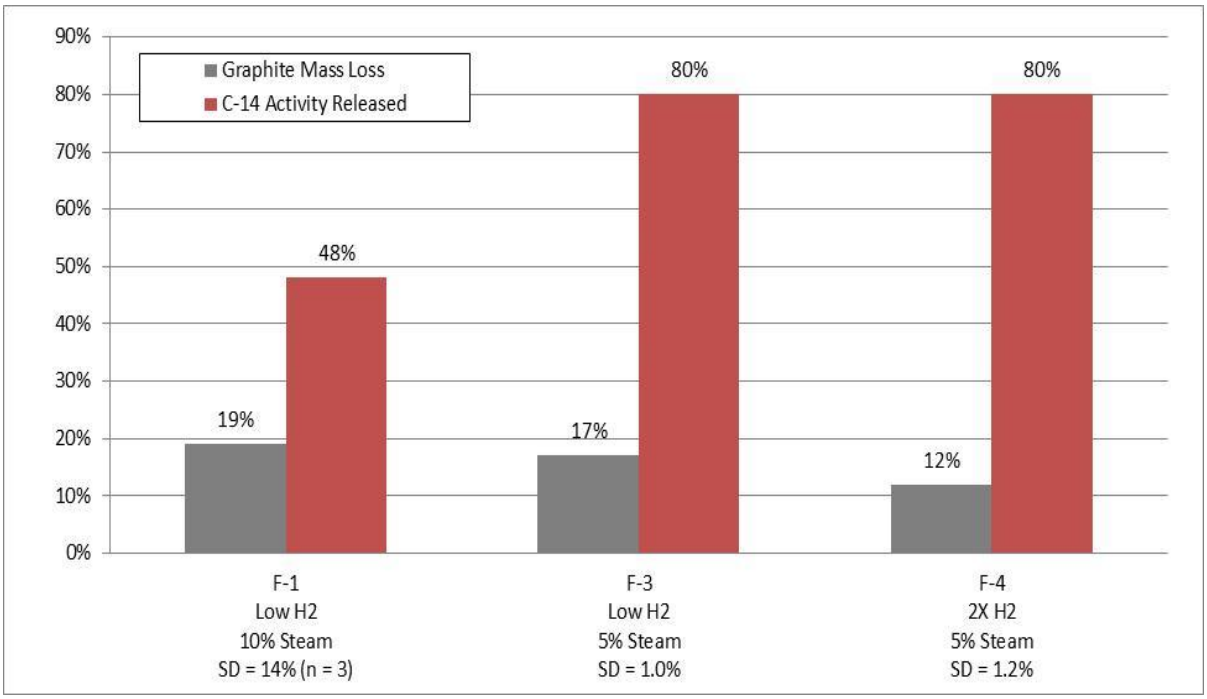

Figure 5.1.3: Fractional C-14 Release and Mass Loss obtained by EDF in various conditions

It has to be underlined that a full understanding if the occurring phenomena still has to be established. From the scientific point of view, since the background is very little on the specific case, a phenomenological approach has been established. The preliminary results reported in Fig. 5.1.3 are highlighting the followings:

- The higher the humidity, the higher the mass loss and the lower is the selectivity of C-14 removal.
- Relatively high selectivity of C-14 removal is achieved with 5% of steam (further information are not available) and 1300 °C.
- The effect of hydrogen on tritium removal is not reported; however, it was reported that nearly 100% of H-3 was removed with small mass loss. For what concerns C-14 removal, it seems that a more reducing environment is favorable; however, further investigations should clarify this observation.

Enrichment factors obtained by EDF investigations ranged from 2.5 till 6.7 (overall carbon atoms removed against total carbon removed). Kinetic studies on the radionuclide releases were not performed.

5.2 Steam Reforming applied in Moscow SIA (Scientific and Industrial Association) "Radon"

Oxidation experiments with i-graphite coming from different sources (Russia) were performed in Moscow Scientific and Industrial Association "Radon".

5.2.1 Investigated Samples

Two i-graphite grades were considered, coming from two reactors: bushing graphite from IPPE and reactor graphite from Kursk NPP: they show different specific activities and radionuclide inventory (see Figs. 5.2.1.a-b and Tab. 5.2.1). It is noticeable how the specific activity of samples differs up to three orders of magnitude, depending on the nuclide, resulting in general higher for the graphite bushing from IPPE; in addition, a marked difference stands on the fuel contamination/activation products, directly correlated to the position in the reactor (no further information are available).

Figure 5.2.1.a-b: i-Graphite from Kunsk NPP, before (a) and after crushing (b)

Figure 5.2.2: i-Graphite bushing from IPPE.

Sample / Nuclide	Graphite Rod	Graphite Rings
	A [Bq/g]	A [Bq/g]
^{60}Co	28.8	$3.31 \cdot 10^3$
^{137}Cs	$2.27 \cdot 10^3$	60
^{134}Cs	-	10
^{241}Am	47.8	-
^{154}Eu	1.5	-
^{144}Ce	5.3	-
^{14}C	$8.6 \cdot 10^2$	$2.2 \div 3.2 \cdot 10^5$
^{3}H	$7.6 \cdot 10^2$	$1 \div 2.8 \cdot 10^4$
^{239}Pu	37	-
^{54}Mn	-	$1.3 \cdot 10^2$
^{95}Nb	-	10
^{94}Nb	-	70
^{65}Zn	-	$1.1 \cdot 10^2$

Table 5.2.1: Radionuclide inventory of the considered i-Graphite samples

5.2.2 Experimental Setup

An electric oven (Fig. 5.2.3) has been used to perform the thermal decontamination experiments, coupled with washing bottles containing a basic solution in order to collect the released radiocarbon (Fig. 5.2.4). In the case of steam treatment, water vapour was produced directly at the inlet of the oven; at the outlet the condensate was captured and washing bottles with basic solution collected the released radiocarbon (Fig. 5.2.5).

Figure 5.2.3: Overview of the equipment used for air and steam thermal treatments

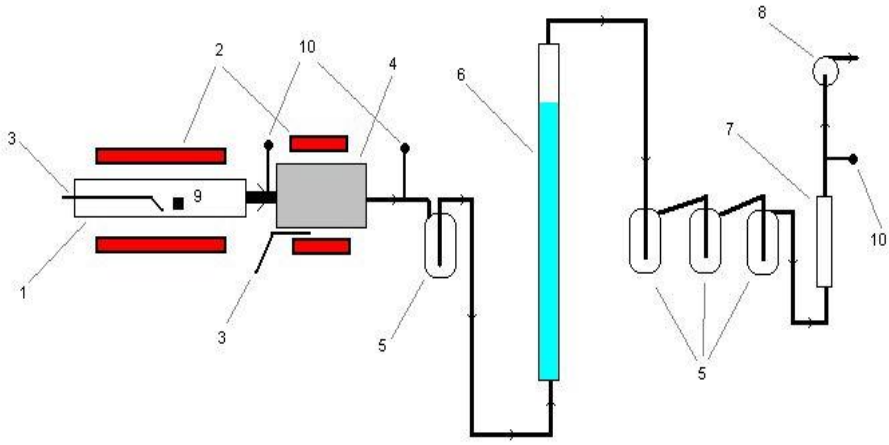

Figure 5.2.4: Schematic view of the experimental setup for the thermal treatment of i-graphite in air

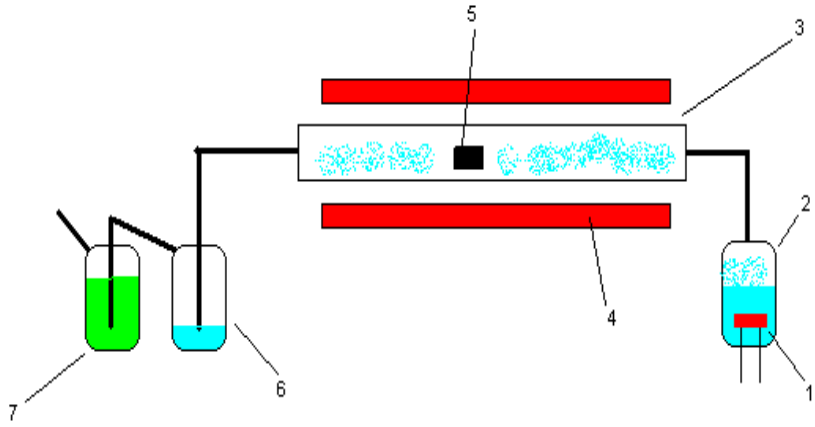

Figure 5.2.5: Schematic view of the experimental setup for the thermal treatment of i-graphite in steam

5.2.3 Experimental Results

In this section the results obtained by SIA ´Radon´ are presented. For completion, all available results from treatments both in air and steam are reported, in order to have a better overview of the graphite behavior.

Air thermal treatments at 650 °C revealed significant mass losses due to the graphite corrosion. However, after 28 hours of treatment, graphite brushing from IPPE revealed a fractional removal of 90% for C-14: such a result is remarkable; however, the mass loss has to be considered: 35%. It corresponds to a C-14 enrichment factor of about 2.6, i.e. for every atom of C-12 released, 2.56 atoms (as a mean) of C-14 are removed. From an industrial point of view it is not clear whether this method could be applied as it is, since the final purpose is to obtain a good selectivity on the decontamination together with low mass losses.

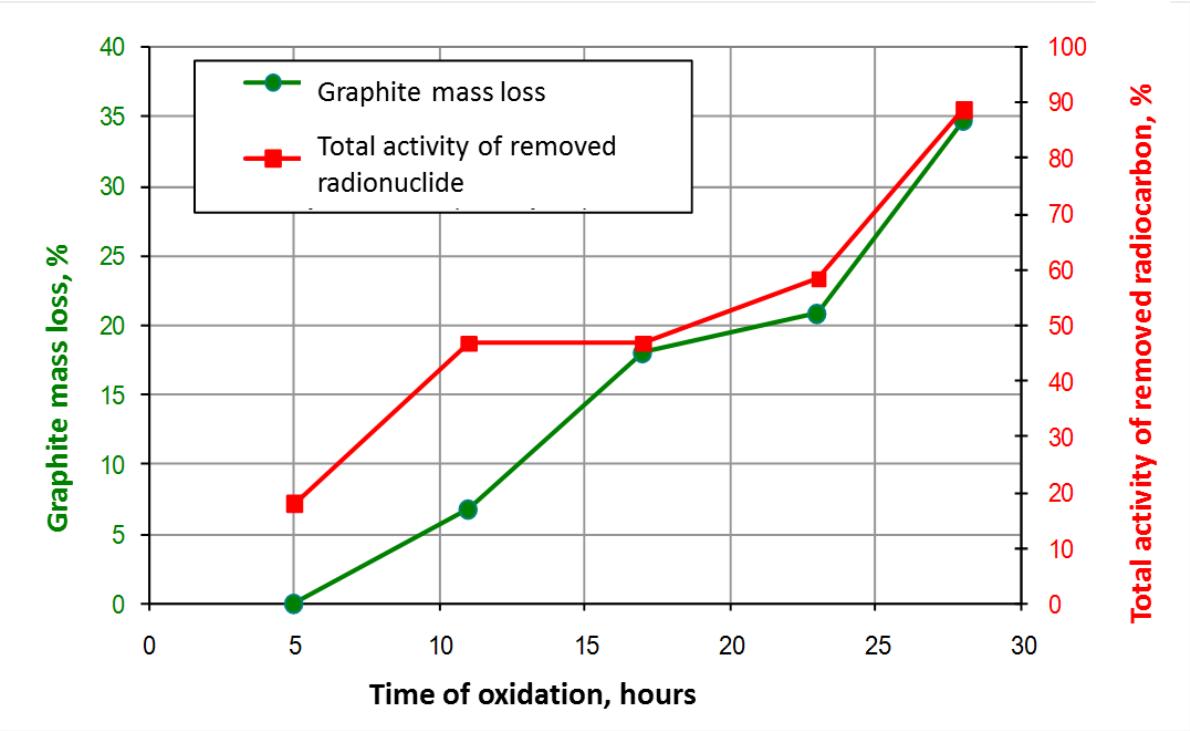

Figure 5.2.6: C-14 fractional release and mass loss against treatment time in air at 650 °C, IPPE graphite.

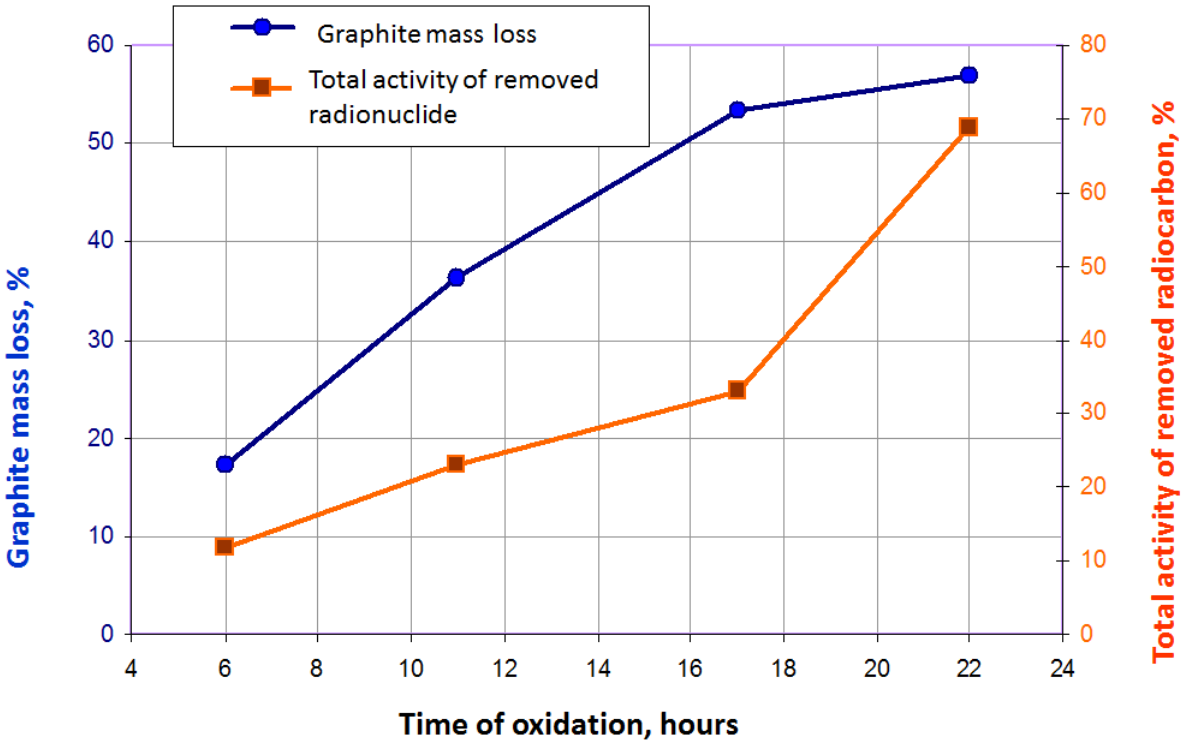

Figure 5.2.7: C-14 fractional release and mass loss against treatment time in air at 650 °C, Kunsk NPP graphite.

Kursk NPP graphite showed a fractional removal of 70% for C-14 with a mass loss of about 57%, i.e. an enrichment factor of about 1.25, much lower than the previous case.

The different behavior of different i-graphite is evident when Figures 5.2.6-7 are compared: under the same conditions, INNP graphite revealed a higher selectivity on the removal of C-14 compared to the results obtained for Kunsk NPP graphite. The reasons behind this fact are various, correlated to the sample history: manufacture, irradiation conditions, storage after irradiation, cutting technique, etc.

For what concerns steam treatment, the same i-graphite were used. In the case of Kunsk NPP graphite, some nuclides with their activities, collected in the water vapour condensate at the oven outlet, are reported in Tab. 5.2.2. Fractional removals values are not available at the present state. The Temperature applied during the steam treatment was 700 °C.

In the case of steam reforming of IPPE graphite, a 24 h treatment at 700 °C removed 20÷50% of C-14 with a mass loss up to 10%. No further data is available.

Total treatment time [hours]	Total activity [Bq]				
	^{3}H	^{14}C	^{137}Cs	^{60}Co	^{65}Zn
15	3400	550	10	20	210
24	-	-	10	30	250

Table 5.2.2: Nuclides and activities collected in the condensate outside the treatment chamber, treatment temperature of 700 °C, Kunsk NPP graphite.

For what concerns the Russian graphite, the conducted research allowed to state that ^{3}H and ^{14}C content in samples of reactor graphite with different irradiation history can vary significantly. In addition, ^{36}Cl is insignificant both for samples from IPPE and Kursk NPP. Oxidation experiments of graphite samples in air flux at a temperature of 600-650 °C allowed to remove more than 90% of Radiocarbon with mass loss not exceeding 20% for IPPE and 55% for Kunsk NPP graphite, referring to the same treatment time and conditions. The necessary duration of treatment significantly depends on graphite irradiation history. Thus for Kursk NPP graphite samples about 20-30 hours of treatment showed to remove more than 90% of ^{14}C, while graphite samples from IPPE required 30-50 hours (depending on temperature). Oxidation of graphite samples in air at temperatures below 600 °C did not result in significant removal of ^{14}C and ^{3}H.

Concerning water vapour thermal treatments, IPPE graphite samples treated for 24 hours at 700°C resulted in a removal of 20-50% of ^{14}C with a graphite mass loss within 10%. The possibility of effective catalytic oxidation and purification of off-gases after graphite oxidation in air flux has been validated: the fraction of CO_2 absorbed by Sodium Hydroxide exceeded 97%.

6. Summary and Outlook

The main goal of this deliverable was to estimate decontamination factors of irradiated nuclear graphite by steam reforming in order to establish a better understanding of its behavior under thermal treatment.

Before working with irradiated graphite, operational conditions were tested with virgin graphite samples. This step was necessary to understand how the furnace would have reacted to the usage of graphite samples; the humidity generator WetSys was tested too in this ambit. After having performed several experiments with non-irradiated graphite, the furnace outlet was connected to the bubblers (washing bottles) in order to collect the released radionuclides.

The uncertainties of the measured data were estimated: about 5% for the tritium measurements and about 10% for ^{14}C measurements. These uncertainties have to be considered for the analysis and interpretation of the gathered data.

The experimental parameters used for Merlin graphite were the following:

- Temperature: 1000 °C,
- absolute humidity: 10 g/kg
- treatment time: 4 h (Merlin-1) and 10 h (Merlin-2, Merlin-3)
- gas flow: 25 mL/min,

Most of the experiments were performed without any leakage or failure, leading to the following decontamination factors (DF) for samples Merlin-1 and Merlin-2; values for Merlin-3 were estimated (Table 5.1).

Merlin-1	**Merlin-2**	**Merlin-3**
• DF(^{3}H) = 3.7	• DF (^{3}H) = 13.4	• DF (^{3}H) ≈ 22.3
• DF (^{14}C) = 1.2	• DF (^{14}C) = 1.4	• DF (^{14}C) ≈ 2.2

Table 5.1 : Decontamination factors for Merlin Graphite treated with steam at 1000°C

The decontamination factors are quite low but, nevertheless, higher than the ones achieved with other methods (see appendix A.2): the steam treatment seems to be promising. However, there are still several factors (temperature, humidity, treatment duration) that must be optimized in order to obtain higher decontamination factors.

The second treatment of Merlin-3 sample failed: an uncontrolled gas leakage occurred, making it impossible to determine precisely the amount of released radionuclides; an indicative estimation has been performed.

The experimental parameters used for Saint Laurent A2 graphite were the following:

- Temperature: 1000 °C,
- absolute humidity: 10 g/kg
- treatment time: 10 h (SLA2 R1, SLA2 R4)
- gas flow: 60 mL/min

The experiments were performed without any leakage or failure, leading to the following DF for samples SLA2 R1 and SLA2 R4:

SLA2-R1	**SLA2-R4**
• DF(^{3}H) = 1.44	• DF (^{3}H) = 2.27
• DF (^{14}C) = 1.03	• DF (^{14}C) = 1.08

Table 5.2 : Decontamination factors for SLA2 Graphite treated with steam at 1000°C

It is noticeable how higher DFs were achieved with the most irradiated graphite. A temperature effect under irradiation could be a reason for this, since the sample SLA2R1 was irradiated at higher temperatures than SLA2R4. However, since SLA2R1 was irradiated at 443°C and SLA2R4 at 391°C, no reactions are expected between CO_2 and graphite; moreover, it is hypothesized that a temperature difference of about 50°C is not significant for the reaction CO_2-graphite in the above-cited temperature range. Another fundamental factor that has to be considered is the radiolytic corrosion together with neutron radiation damage, expected higher for SLA2R4 than SLA2R1 since the former was in the middle of the core (h = 5120 mm) and the latter was at the bottom (h = 1680 mm). In line of principle, a higher reactivity would be expected from the most irradiated sample due to the higher specific surface area caused by radiation damage. Accordingly, it is very probable that the most significant influence on the reaction rates and removal behavior of ^{14}C and ^{3}H from SLA2 graphite is the neutron fluence, coupled with the radiolytic corrosion: such corrosion is higher in SLA2 R4 than in SLA2 R1 and correlates directly to the neutron fluence. In fact, on the one hand a higher surface area is produced due to neutron irradiation, while on the other hand a corrosion process is taking place, leading to releasing of radionuclides in situ. An indication on the importance of the two

effects, coming from the results obtained in FZJ, seems to point in the direction of neutron fluence predominance; however, more experiments are necessary in order to confirm or discard such a statement.
For what concerns ^{3}H, the DF for R1 is 1.44 against 2.27 for R4. Similarly, for ^{14}C, R1 showed a DF of 1.03 and R4 1.08. A higher decontamination could, then, be correlated with higher neutron fluence.

However, it has to be underlined that the presented results are not significant from the statistic point of view and they cannot be considered as representative of the whole graphite in the same position in the SLA2 reactor. Future investigations should focus on this topic in order to better characterize the graphite behavior in relation with its position in the reactor, considering the atmosphere and the neutron flux.

Several conditions revealed to heavily affect the behavior of any i-graphite. Up to now, no literature reported a correlation among radiolytic corrosion and ^{3}H / ^{14}C removal. Further studies should focus on that way in order to better understand the removal mechanisms and radionuclide distribution inside the reactor in correlation with the history of the graphite.
A further approach for the future, for what concerns the treatment process, could be fixing a treatment time longer than 10 hours and optimizing the experimental parameters (as temperature and humidity) in order to decontaminate the samples to a maximum amount in the given time.

A comparison of the results obtained in different institutes allowed confirming that any i-graphite is a unique case, with a treatment behavior that is strongly depending on its entire history. From the point of view of Tritium removal, the fact that it depends mainly on temperature seems to be confirmed: the higher the temperature, the higher the removal, in particular showing a diffusion-like process. This finding is in line with the model proposed by Atsumi [ATS11]. The presence of water vapour or hydrogen showed to enhance significantly the Tritium removal on the one hand, but diluting it on the other hand, so an inert gas roasting process is strongly advised in case a steam/hydrogen treatment were chosen to be applied. Concerning radiocarbon, all institutes (EDF, FZJ, SIA ´Radon´) verified the correlation among

its removal and the presence of oxidants. Optimization of the treatment parameters still has to be performed in order to results in the highest possible decontamination in a limited amount of time with a contemporary limited mass loss. Anyway, for the steam treatment but not only, the removal efficiencies vary widely from one i-graphite to the other, depending on C-14 source, distribution and speciation, depending in turn on many influencing variables that marked the lifetime of any specific sample. The speciation, location, bonds and release mechanism(s) of C-14 have to be better understood in the next future: up to now phenomenological investigations have been mainly performed, also due to the consistent amount of variables difficult to separate and due to the lack of a proper former knowledge in literature. The way to undertake, from a scientific point of view as first, not neglecting the industrial point of view as second, is the systematic separation of the influencing variables together with the establishment of a dedicated multi-scale model that is taking into account the major influencing factors that are resulting at the end in the observed phenomena.

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FZJ1 Forschungszentrum Jülich (Research Center Jülich) FRJ-1 Merlin
http://www.fz-juelich.de/gn/DE/Leistungen/NukleareProjekte/VorhabenProjekte/FRJ-1/Forschungsreaktor_MERLIN.html

FZJ2 Forschungszentrum Jülich (Research Center Jülich) FRJ-2 DIDO
http://www.fz-juelich.de/gn/DE/Leistungen/NukleareProjekte/VorhabenProjekte/FRJ-2/frj-2_node.html

FZJ3 Forschungszentrum Jülich (Research Center Jülich) FRJ-2 Dismantling
http://www.fz-juelich.de/portal/DE/UeberUns/Verantwortung/Aktuelles/doc/12-09-28dido-rueckbau.html

BfS Bundesamt für Strahlenschutz (Federal Office for Radiation Protection)
http://www.bfs.de/en/endlager/einfuehrung.html

HUT Hutchinson Encyclopaedia
http://www.talktalk.co.uk/reference/encyclopaedia/hutchinson/m0025923.html

A. Appendix

A.1 Activity inventories of some nuclear graphite

A.1.1 Irradiated DIDO graphite

Radionuclides	Activity [Bq/g]	Half-life [a]
^{3}H	2.4 E+06	12.32
^{14}C	9.8 E+04	5730
^{55}Fe	6.9 E+03	2.73
^{60}Co	7.4 E+03	5.27
^{90}Sr	0.0 E+00	28.5
^{134}Cs	2.7 E+02	2.1
^{137}Cs	7.5 E+01	30.2
^{133}Ba	1.8 E+02	10.54
^{152}Eu	0.0 E+00	13.3
^{154}Eu	2.3 E+03	8.8
^{155}Eu	1.3 E+03	4.8

Table A.1: Activity of DIDO graphite (Date: June 15, 2011)

A.1.2 Irradiated Merlin graphite

Radionuclides	Activity [Bq/g]	Half-life [a]
^{3}H	1.5 E+03	12.32
^{14}C	4.3 E+02	5730
^{55}Fe	3.3 E+01	2.73
^{60}Co	2.7 E+00	5.27
^{90}Sr	0.0 E+00	28.5
^{134}Cs	0.0 E+00	2.1
^{137}Cs	0.0 E+00	30.2
^{133}Ba	9.9 E+00	10.54
^{152}Eu	4.9 E+02	13.3
^{154}Eu	2.6 E+01	8.8
^{155}Eu	0.0 E+00	4.8

Table A.2: Activity of Merlin graphite (Date: June 15, 2011)

A.1.3 Irradiated Saint-Laurent A2 graphite

Radionuclides	Activity [Bq/g]	Half-life [a]
^{3}H	3.4 E+04	12.32
^{14}C	4.4 E+04	5730
^{55}Fe	0.0 E+00	2.73
^{60}Co	3.3 E+04	5.27
^{90}Sr	0.0 E+00	28.5
^{134}Cs	1.1 E+01	2.1
^{137}Cs	6.9 E+01	30.2
^{133}Ba	8.9 E+01	10.54
^{152}Eu	0.0 E+00	13.3
^{154}Eu	1.5 E+02	8.8
^{155}Eu	4.2 E+01	4.8

Table A.3: Activity of Saint-Laurent A2 graphite (Date: June 15, 2011)

A.1.4 Irradiated RBMK graphite

Radionuclides	Activity [Bq/g]	Half-life [a]
^{3}H	0.0 E+00	12.32
^{14}C	2.4 E+04	5730
^{54}Mn	2.1 E+00	0.86
^{55}Fe	0.0 E+00	2.73
^{60}Co	3.1 E+01	5.27
^{90}Sr	0.0 E+00	28.5
^{134}Cs	0.0 E+00	2.1
^{137}Cs	6.7 E-01	30.2
^{133}Ba	0.0 E+00	10.54
^{152}Eu	0.0 E+00	13.3
^{154}Eu	0.0 E+00	8.8
^{155}Eu	0.0 E+00	4.8

Table A.4: Activity of RBMK graphite (Date: June 15, 2011)

A.2 Summary of thermal treatments with decontamination factors

Revision date: 25/02/2013

Exp. No.	Sample	Irradiation conditions		Experimental conditions				Mass loss [%]	Release [%]						Decontamination factor[4)]	
		Cool. gas	T [°C]	Treat. gas	T [°C]	Treatment time [h]			HTO	HT	^{3}H total	$^{14}CO_2$	^{14}CO	^{14}C total	^{3}H	^{14}C
						Heating	Isothermal									
V4	Merlin	Air	RT	N_2 + 0.14% O_2[1)]	1300	0	10	0.89	85.9	7.7	93.6	3.4	2.5	5.9	15.4	1.05
V5	Merlin	Air	RT	N_2 + 1% O_2	900	3	2.5	6.64	10.1	0.2	10.3	8.6	3.3	11.9	1.04	1.06
V6	Merlin	Air	RT	N_2 + 1% O_2	700	2.5	7.75	7.22	26.5	0.2	26.7	14.5	7.3	21.8	1.26	1.19
V7	SLA2 9260	CO_2	258.5	N_2 + 0.14% O_2[1)]	1300	0	10.5	0.91	65.0	0.2	65.2	1.4	0.6	2.0	2.85	1.01
V8	Merlin	Air	RT	N_2 + x% O_2[2)]	1300	0	21	5.12	65.6	31.3	96.9	2.5	8.2	10.7	30.4	1.06
V9	Merlin	Air	RT	Pure N_2	1100	3.75	20	0.20	4.6	56.3	60.9	0.12	2.0	2.1	2.55	1.02
V10	Merlin	Air	RT	Pure N_2	1100	3.75	25.5	0.01	1.2	0.09	1.3	1.5	1.3	2.8	1.01	1.03
V11	Merlin	Air	RT	Pure N_2	1100	3.75	20.5	0.16	15.2	21.1	36.3	0.6	1.4	2.1	1.57	1.02
V12	SLA2 9260	CO_2	258.5	Pure N_2	1100	3.75	20.5	0.45	13.3	7.3	20.6	0.4	2.0	2.4	1.25	1.02
V13	Magnox	CO_2	270	Pure N_2	1100	3.75	11	0.14	1.8	0.8	2.6	0.5	1.9	2.4	1.02	1.02
V14	Merlin	Air	RT	N_2 + 0.1% O_2[3)]	750	2.5	5	0.22	1.1	0.1	1.2	0.8	0.4	1.2	1.01	1.01
V15	Magnox	CO_2	270	N_2 + 0.1% O_2[3)]	900	3	5	0.70	5.2	0.5	5.7	35.6	22.1	57.7[5)]	1.05	2.34
V16	Magnox	CO_2	270	N_2 + 0.3% O_2[3)]	900	3	5	3.90	9.0	0.1	9.1	3.8	1.3	5.1	1.06	1.01
V17	Merlin	Air	RT	N_2 + 0.3% O_2[3)]	900	3	5	1.62	30.0	0.07	30.1	9.9	4.1	14.0	1.41	1.14
V18	Merlin	Air	RT	N_2 + 0.3% O_2[3)]	900	3	5	2.72	33.0	0.4	33.4	4.7	0.9	5.6	1.46	1.03
V19	SLA2 9260	CO_2	258.5	N_2 + 0.3% O_2[3)]	900	3	5	2.43	10.3	0.06	10.4	2.8	0.6	3.4	1.09	1.01
Merlin-1	Merlin	Air	RT	Ar + steam (1.6 kPa)	1000	3.25	4	1.58	58.0	15.4	73.4	12.1	8.0	20.1	3.69	1.23
Merlin-2	Merlin	Air	RT	Ar + steam (1.6 kPa)	1000	3.25	10	3.64	74.7	18.2	92.9	16.3	12.7	29.0	13.4	1.36
FH1	SLA2 5120	CO_2	391.5	Ar	1000		40	0.70			29.4			2.4		

RT = Room temperature

Red values: Determined by assuming an averaged initial radionuclide content. Determination of the residual activity of the sample is in progress.

[1)] Ceramic tube with measured ingress of O_2

[2)] New ceramic tube, unknown ingress of O_2

[3)] Quartz tube with defined amount of O_2 in the treatment gas

[4)] The ratio of initial specific radioactivity to final specific radioactivity resulting from a separation process [McGraw-Hill: Dictionary of Scientific and Technical Terms]. 1000 and above is excellent; 10 and below is poor [Hutchinson encyclopaedia].

[5)] Probably a surface contamination

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