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Radionuclide release from contaminated graphite by high temperature pyrolysis

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Radionuclide release from contaminated graphite by high temperature pyrolysis

Executive summary

This report relates to work carried out at ITU Karlsruhe for the CARBOWASTE programme as part of the work package 4 (WP4) to investigate the various pyrolytic treatments (thermal treatments under inert or vacuum atmospheres) and their efficiency in decontaminating the i-graphite samples.
Initially, 2 sorts of i-graphite samples were to be examined by Knudsen cell mass spectroscopy, and with the Kühlfinger (KüFa) facility using longer term testing. As the first samples (Merlin reactor) graphite were too inactive then further transports of samples from Latina were organised as well as preparation of pyrolytic graphite samples from a HTR fuel sample.
Finally testing of all samples by the Knudsen cell was possible but due to breakdown of the KüFa no longer thermal treatments could be carried out.
The Merlin graphite showed too low a level of C-14 to be measurable. Only C-13 could be detected. The releases for D-H/T were at the limits of detection and so little could be deduced. Initial releases (from impurities or deposits in the system) were occurring at ~800-900K.
For the Latina graphite there was also considerable doubt as to the origin of the key mass signals and there are many sources of impurities such as N (amu 14). Initial releases were observed at 720 to 820K; often a sharper first release, then a second broader release from 1000 to 1250K; the latter may be dominated by impurities. Volatilisation from the sample of light gaseous species is most likely to be contained in the low temperature range of releases. Possibly some matrix volatilisation of C-12 was observed at the highest temperatures (>2500K).
The AVR pyrolytic graphite sample was performed in comparison with a blank run. It demonstrated the memory effects (of Cs-133 from a previous test). Nevertheless the sample showed some very sharp releases at around 1000K of most light masses. Cs-137 release was also clearly seen at this temperature range. This suggests that C-14 and other light molecular or volatile species would also be released under the same low temperature conditions as resulted in the Cs-137 release. This is certainly possible if other elements or activation/fission products were not located in the graphite lattice (such as N_2 or C-14). Further testing is need to confirm this.

Revisions						
Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
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1. Objectives of the Task

This investigation on the pyrolysis of irradiated graphite has the objective of ascertaining the possibilities of decontamination by pyrolytic techniques under inert or vacuum atmospheres. In addition information on the location or preferred location of the typical isotopes in irradiated graphite lattice will also enable the mechanism of losses/retention to be better understood. This can also point the way to new techniques or refinements of current decontamination techniques. This in term will reduce the potential source term and requirements and costs of graphite's final storage or offer possibilities of re-cycling.
ITU is contributing to this study by examining the use of high temperature annealing of large samples for longer tem testing (KüFa facility) and smaller samples (Knudsen cell) under vacuum or inert atmosphere. Because of problems in the KüFa facility, the results largely concern the Knudsen cell testing of 3 types of i-graphite.

2. Investigated Samples

2.1 Merlin Graphite

The MERLIN reactor (Medium Energy Research Light-Water-Moderated Industrial Nuclear Reactor, called also FRJ-1) at the research centre of Jülich was a light-water-moderated and -cooled swimming pool reactor. It was built between 1958 and 1962 and was subsequently used for various irradiation experiments, especially in the field of material science. Such reactor implied nuclear-grade graphite in a thermal column (see Figure 2.1.1-a,b) and operated from 1964 till 1985. After 10 years its dismantling began and was completed in 2009: the reactor has been completely decommissioned and reached the so-called “green field” status. The thermal power was initially 5 MW, raised later on up to 10 MW with a thermal neutron flux up to $1.1 \cdot 10^{14}$ n/cm^2·s. The 10 tons of graphite are presently placed in an intermediate storage. Several samples of the thermal column have been used for the investigations on graphite treatments within the scope of this report.[4]

2.1.1 Merlin samples: Origin and preparation

The samples used in the following tests were removed from the thermal columns during the reactor block's demolition. The thermal columns were used to slow down the fast neutrons, released during the nuclear reaction, to thermal neutrons for test purposes. The following figures 2.1.1-a and 2.1.1-b show the reactor block's structure.

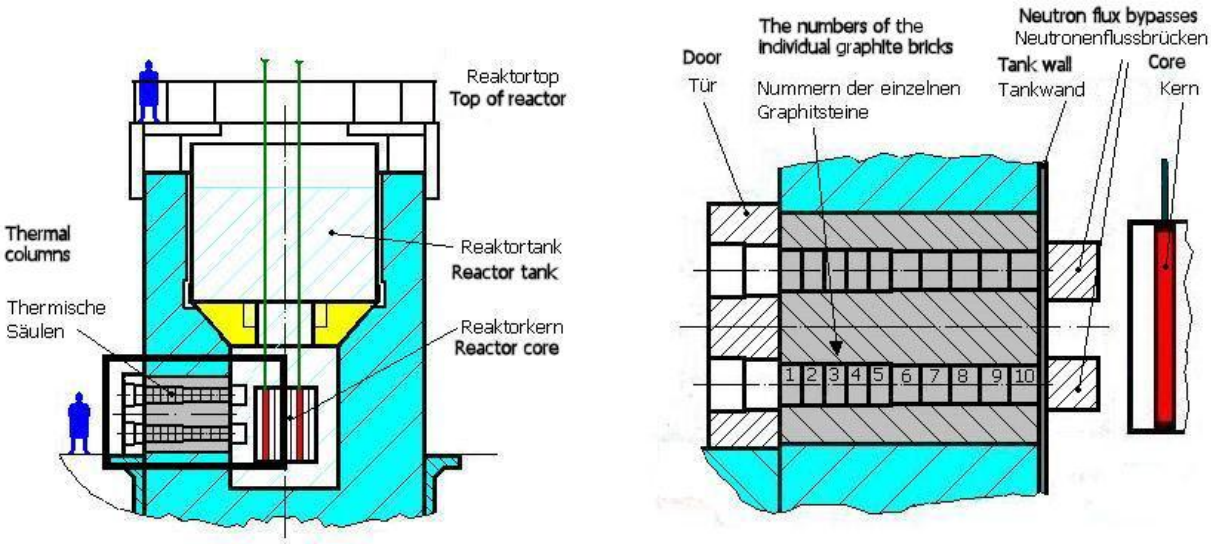

Figure 2.1.1: (a) Cross section of the reactor block (left) and (b) position of the individual graphite bricks inside the reactor block (right)

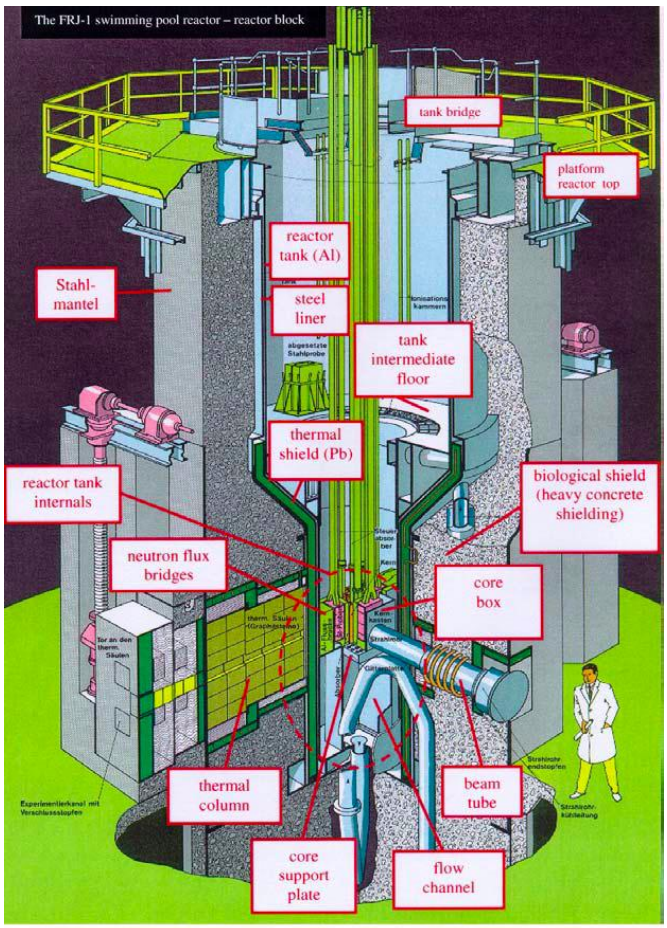

Figure 2.1.2: MERLIN Material Test Reactor (FRJ-1)

A graphite sample from the Merlin research reactor (FRJ-1) was transported to ITU from FZJ in Dec. 2009. The sample, as shown in Fig. 2.1.3, is a block of material with a mass of 320 g; the dimensions are 75×50×50 mm.

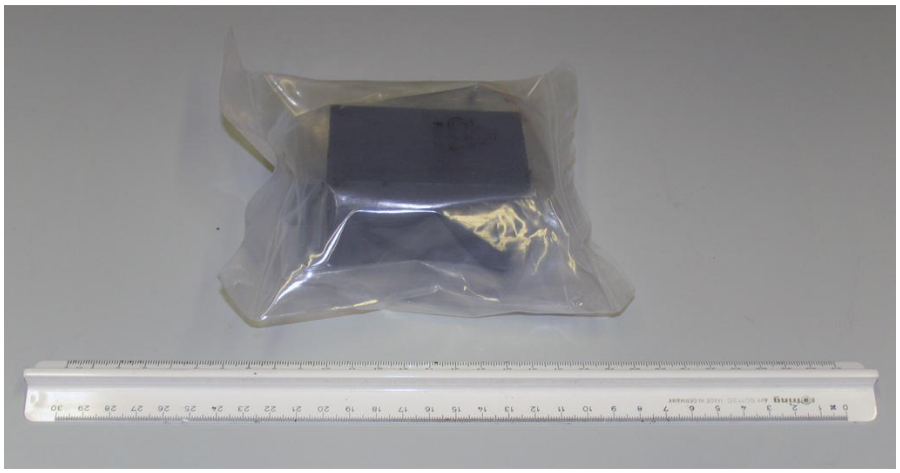

Figure 2.1.3: Graphite block from the Merlin reactor used for the high temperature treatment in Knudsen cell

Table 2.1.1 summarizes the known content of radionuclides in the samples. No indication on the content of ^{36}Cl and ^{129}I is available ; the total activity is about 1.6 MBq.

Nuclide	Activity (Bq)	Quantity (mol)
T	1.1×10^{6}	1.0×10^{-9}
C-14	1.2×10^{5}	5.2×10^{-8}
Fe-55	2.9×10^{4}	6.0×10^{-12}
Co-60	1.2×10^{3}	4.8×10^{-13}
Ba-133	3.3×10^{3}	2.6×10^{-12}
Eu-152	1.5×10^{5}	1.5×10^{-10}
Eu-154	4.2×10^{3}	2.7×10^{-12}

Table 2.1.1 : Content of individual radionuclides in a Merlin irradiated graphite block (320g) according to radiochemical analyses (meas. date: 25.05.2009)

2.2 Latina Moderator Graphite

The Latina NPP is located at Borgo Sabotino-Latina close to the Thyrrenian Sea. The Latina NPP was a CO2 cooled MAGNOX type reactor similar to the Bradwell NPP in UK, using 264 tons of metallic natural uranium as fuel and some 2100 tons of graphite as moderator. It had a nominal thermal power of 705 MW (later on lowered to 640 MW) and a net electrical output of finally some 153 MW. The primary circuit consisted of six cooling sub-circuits with individual gas blowers and boilers for gas/water heat exchange. The three steam operated turbines were driving three turboalternators (plus two auxiliary ones) for electricity generation.[7] The NPP of Latina operated from May 1963 until 1987.

2.2.1 Samples from Latina Nuclear Power Plant

Several samples from irradiated graphite channel bricks and trepanned samples from the decommissioned Italian LATINA reactor that were expected to be approximately one order of magnitude greater in total activity compared to the Merlin samples (see tables 3.5.1-2 below). Samples of virgin graphite block will be available in the next future in order to allow comparisons with the irradiated samples.

Identification code	Dose rate on contact	Size (Ø x h)	Mass
04F04A1/C1	1,6 µSv/h	17 mm x 16 mm	6,2 gr
12F16U2/C4	0,3 µSv/h	17 mm x 14 mm	4,6 gr
12F16U2/I3	0,3 µSv/h	17 mm x 14 mm	3,1 gr
12F16U2/S4	0,3 µSv/h	17 mm x 14 mm	4,1 gr
CELL B – n.2	0,6 µSv/h	17 mm x 18 mm	7,1 gr

Table 2.2.1: Dose Rates of Latina i-graphite samples (trepanned samples & channel bricks) selected for ITU (Mar '12). Activity & composition from ENEA (SOGIN) Italy.

Isotope	Specific Activity (Bq/g)
H-3	3,0E+04 Bq/g
C-14	3,5E+04 Bq/g
Cl-36	3,0E+01 Bq/g
Co-60	1,7E+02 Bq/g
Cs-137	2,0E+01 Bq/g
Ba-133	3,3E+01 Bq/g
Eu-154	8,5E+01 Bq/g
Eu-155	1,5E+01 Bq/g

Table 2.2.2: Specific activities of the main isotopes of Latina irradiated graphite samples selected for ITU (Mar '12). Alfa emitters may be present at concentrations <0,5 Bq/g. Activity & composition from ENEA (SOGIN) Italy.

These samples were due to be transported in the period Sept-Dec'12, but due to delays were expected to be finally transported to ITU in March'13. In view of these delays, it was decided to find alternative samples from HTR fuel elements (see next section 2.3.1).

2.3 AVR (Arbeitsgemeinschaft VersuchsReaktor)

The AVR (Arbeitsgemeinschaft VersuchsReaktor) was the first experimental high temperature reactor of pebble bed type worldwide on industrial scale. Main aim of this experimental reactor was the test of the pebble bed core concept and the test of many different types of pebble shaped fuel elements. It started working in 1967 and its definitive shut-down dates back to 1988. The electrical power output was 15 MWe (46 MW_{th}). It was helium cooled and high-purity graphite was used both as moderator and reflector. In particular, the present paper deals

with some investigations on the reflector graphite. The bottom, side and top reflectors as well as the so-called "reflector noses" consisted of polycrystalline graphite (needle-coke graphite, ARS/AMT grade made by SIGRI-Elektrographit [10]), chosen due to its chemical and physical properties and behaviour under fast neutron irradiation. The graphite reflector wall of 50 cm thickness [9] surrounded the reactor core containing the spherical fuel elements (see Fig. 2.3.1). The graphite brick reflector vessel is enclosed in a 50 cm envelope made of "baked carbon" bricks ("early stage graphite", with larger amounts of impurities), which provides shielding and thermal insulation. Double wall steel liner surrounds all the ceramic structure. The bottom and top reflector consist also of graphite, surrounded by "baked carbon" bricks. A peculiarity of the here presented graphite is the method of manufacture: extrusion was implied, leading to highly anisotropic properties of the final product.

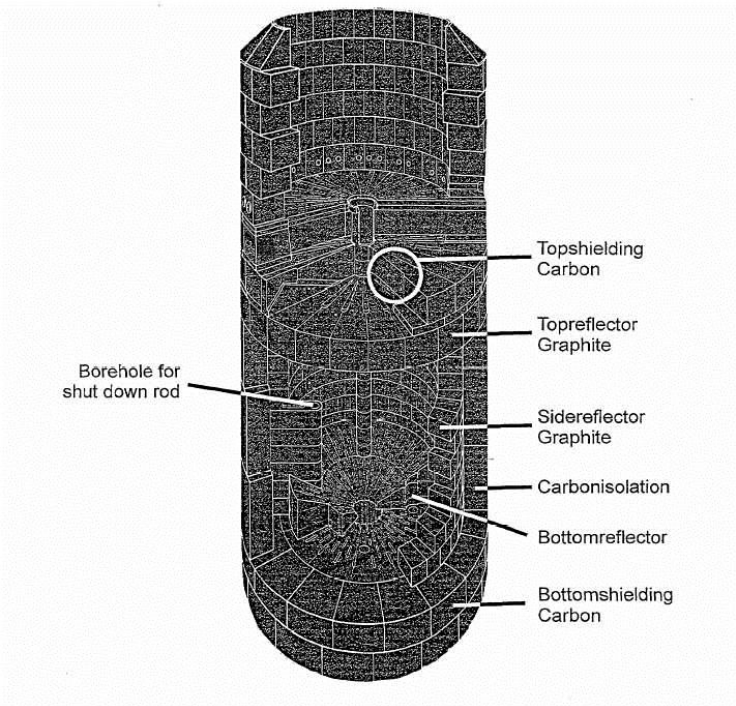

Figure 2.3.1: Internal structure of AVR's core and heat exchanger chamber

2.3.1 Graphite samples from AVR Pebble

ITU had some AVR pebbles for the HTR reactor in Jülich that had been irradiated to various burn-ups in the High Flux Reactor in Petten (EU1 bis irradiation). It was therefore decided to take samples of the outer pyrolytic graphite layer (several mm thick) from one pebble at ITU (No.3) and subject these irradiated graphite samples to a heating regime up to 1500°C in inert atmosphere and determine the resulting loss of activity. Knudsen Cell measurements will also be made on these samples before and after heating.
The following irradiated graphite samples (~4mm thick) were extracted from the pebble:

- Carbowaste 1 (0.4 $mSv.h^{-1}$) –outer PyC graphite shell only.
- Carbowaste 2 (11 $mSv.h^{-1}$) –outer Pyrolytic graphite shell + fuel traces on the inner side

Figure 2.3.2 shows a cutaway view of the pebble produced after 1981 (that weighs approximately 200g) and illustrates the graphite shell that has been extracted as a test-piece.

The average thickness of this outer graphite shell is nominally 5mm, but in practice was found to be 6,2mm [1].

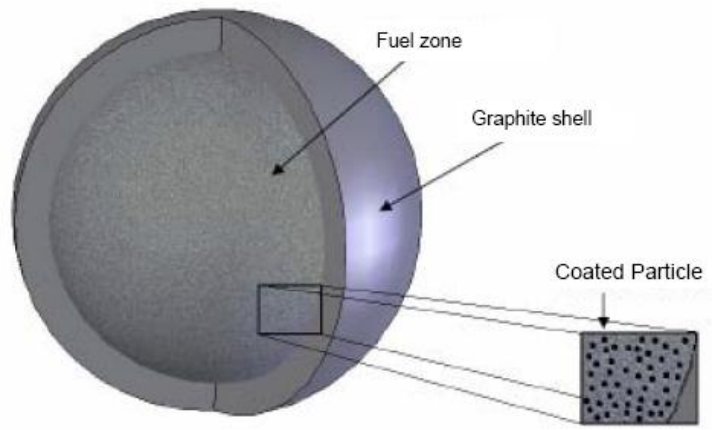

Figure 2.3.2: Cutaway illustration of HTR fuel element showing the outer graphite shell to be sampled.

Photos of the ″Carbowaste 1″ & ″Carbowaste 2″ samples prepared for the KüFa annealing tests are shown in Figures 2.3.6-7.

Sample Preparation

A cylindrical carrot was extracted from the spherical fuel element by drilling through an arbitrary diameter of the pebble with a hollow drill, as shown in Figure 2.3.3. The outer diameter of the drill was 12 mm, the inner diameter ≈ 10.5 mm. The length of the carrot was initially identical to the diameter of the pebble (60 mm); however, a thin section (≈ 3 mm) from the fuel-free graphite zone broke off as the mesh pierced through the far end of the fuel element.

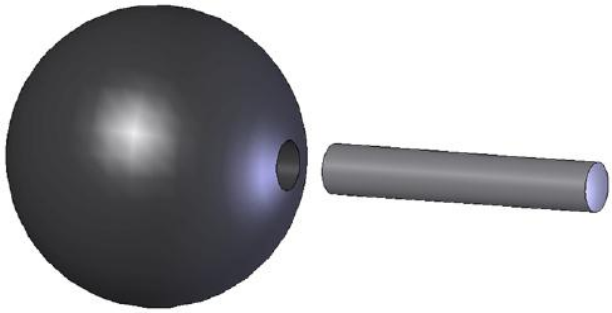

Figure 2.3.3: Sketch of drilled fuel element with extracted carrot.

The carrot was cut in four positions placed at distances ≈ 15.0 mm, ≈ 24.3 mm, ≈ 39.8 mm, and ≈ 50.1 mm from one of the pebble faces, as indicated in the cutting plan shown in Figure 2.3.4. Since it was not possible to remove the carrot from the hollow drill, the drill was cut along with the carrot and effectively protected the sample during the segmenting process.

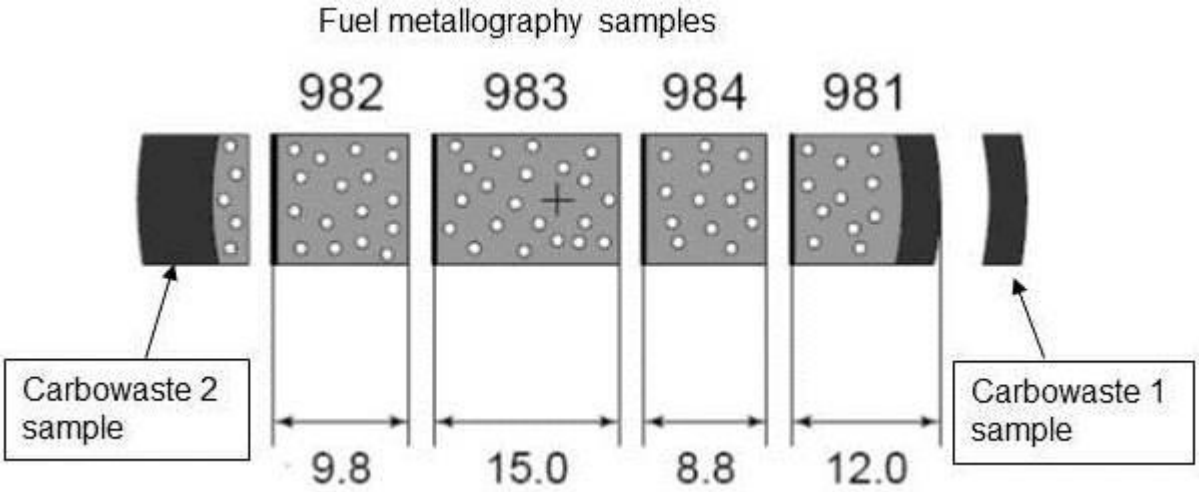

Figure 2.3.4: Cutting plan for the cylindrical carrot obtained from fuel element HFR-EU1bis/3.

The thick lines indicate the faces of the sample disks that are directed towards the microscope. The obtained cylindrical samples were labelled from 981 to 984 and embedded in sample holders that had been custom-fabricated for each sample. Figure 2.3.5 shows photographs of all four samples in their respective sample holders taken with a video camera prior to being embedded in resin. Some individual CPs can be clearly distinguished in Samples 983 and 984. Sample 984 was examined, after grinding, polishing and Au coating, with the SEM. Taking into account the cutting disk's thickness of 0.5 mm, its upper surface was located at a depth of about 24.3 mm from the surface of the pebble.

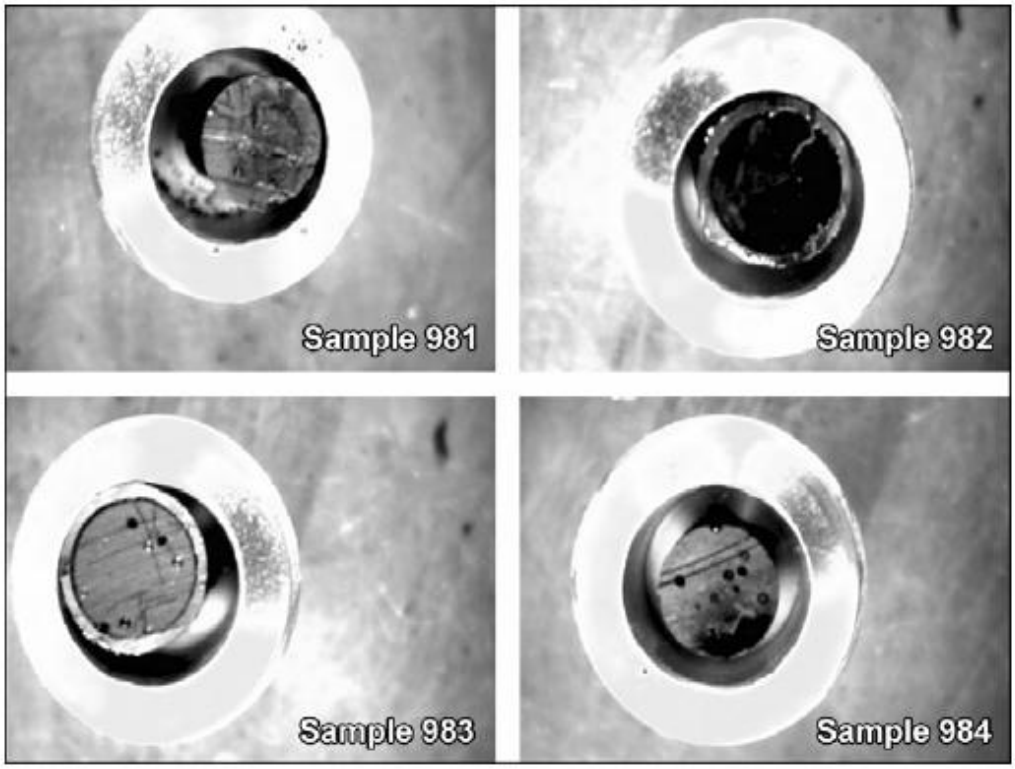

Figure 2.3.5: Carrotage samples placed in the sample holders, prior to embedding in resin. The respective sample numbers are indicated in the lower right corner of each image.

The two samples from the external graphite surfaces of the AVR pebble are shown in Figs. 2.3.6 & 2.3.7. They are approximately 1cm diameter and 4mm thick. A small amount of graphite powder was scraped off "Carbowaste 1" for Knudsen cell testing, but because of the hard steel ring surrounding the "Carbowaste-2" sample it was necessary to drill out a small hole in the centre to get a pre-test sample for Knudsen cell testing (see figure 2.3.7).

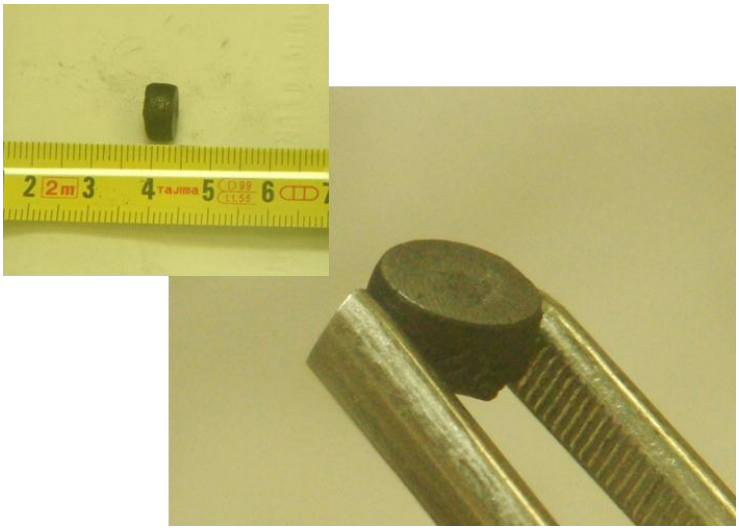

Figure 2.3.6: Photos of the surface carrotage sample "Carbowaste-1". The outer surface is shown in the large photo; the thickness of 4mm is seen in the inset photo.

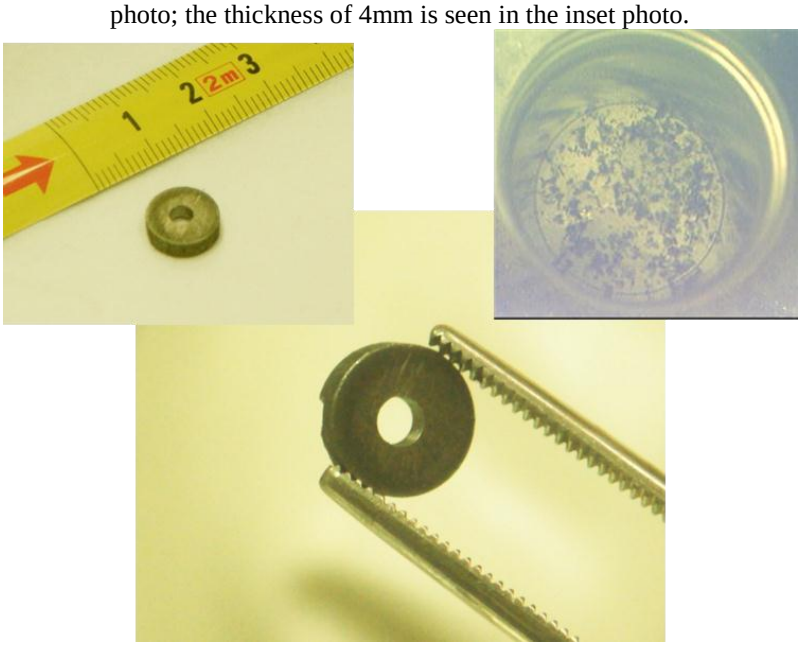

Figure 2.3.7: Photos of the surface carrotage sample "Carbowaste-2". The diameter of 1 cm is shown in the inset photo. The sample has an outer steel ring from the hollow drill bit when the sample was cut out. A pre-test Knudsen cell sample was drilled out from the centre. The left-hand photo shows some grains of the pre-test Knudsen cell sample.

3. Description of Experimental Facilities

3.1 Knudsen Cell at ITU

3.1.1 Description of Knudsen Cell facility

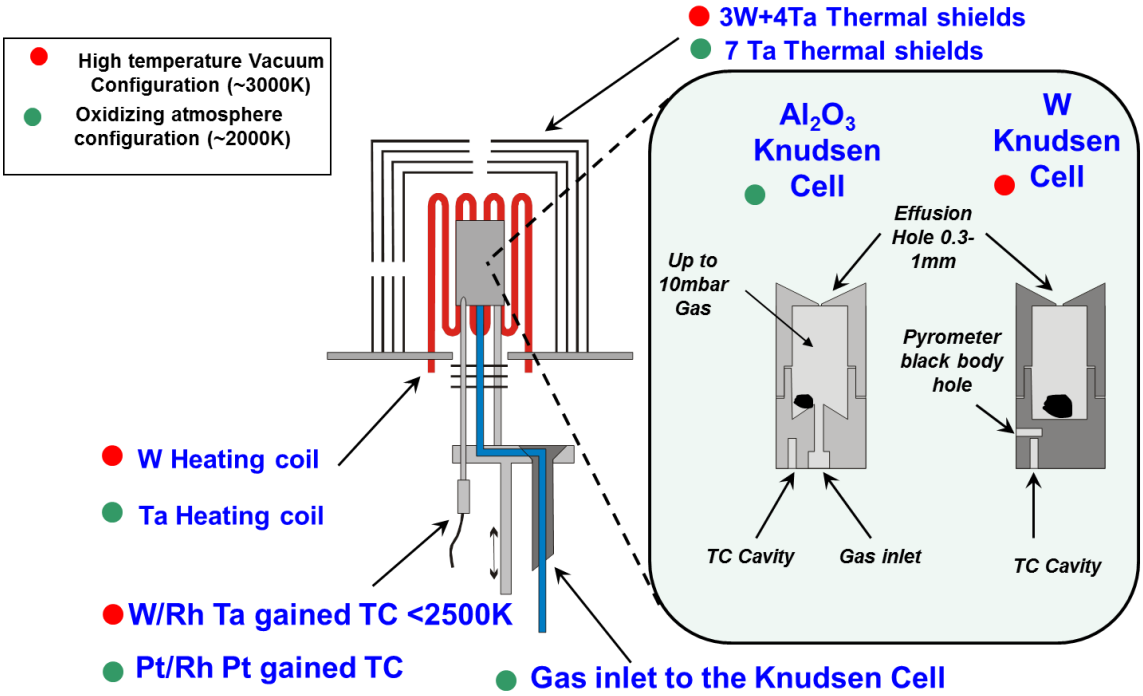

Figure 3.1.1 Schematic overview of the Knudsen Cell for analysis of radioactive samples

The Knudsen Cell is a covered cell of inert material (either a high melting metal (Ta or W)) or ceramic (Al_2O_3) with a small sample (typically from 1g to 10mg) enclosed (see Fig. 3.1.1). Often a small amount of reference material (eg. few milligrams of Ag) is added to the cell with the sample. After loading the cell, it is placed in position and the system put under high vacuum or under a very low pressure of a controlled gas. The cell itself can be heated by the surrounding heating element in a controlled ramp or series of plateaux up to 2700K. The cell has a small aperture (effusion hole) at the top from which the vaporising material can escape and pass into the electric & magnetic fields of an attached mass spectrometer that analyse the vapours. At a fixed temperature, the vapours are in equilibrium with the solid in the cell so that, in the case of pure elements, the vapour pressure of the element can be derived; in the event of mixtures of elements then information as to their relative volatility can be ascertained.

3.1.2 Performance of Experiments

3.1.2.1 Experiments with Merlin Graphite

Typically 60 mg specimens cut or scraped from the Merlin graphite block were subjected to a steady temperature ramp up to 2700K in a Knudsen cell apparatus under high vacuum. The adjacent mass spectrometer could analyse the vapour released during the temperature ramp. The main nuclides of interest were ^{3}H, ^{14}C, ^{36}Cl, ^{129}I. The purpose of these preliminary tests was to ascertain if the apparatus would be suitable to analyse the release behaviour of these nuclides, even at low levels, from a graphite sample.

3.1.2.2 Experiments with Latina Graphite

Irradiated graphite samples from 6 locations of the Latina reactor were delivered. On noting the low activity levels and low dose rates of the samples and given the low Knudsen cell signals obtained from the Merlin graphite, it was decided to examine the most active sample first to have the best chance of a good result. This was 04F04A1/C1 one of the channel bricks which had a 1,6 $\mu Sv.h^{-1}$ contact dose rate. The pellet–shaped sample was removed from its container and a small amount of powder (~50mg) was scraped off with a spatula and placed in marked, aluminum container for transfer to the Knudsen cell in another laboratory where the sample was placed under vacuum before undergoing a steady temperature ramp to 2400K. Mainly the light isotopes upto 50 were examined to see if the volatilization C or its compounds could be discerned. Further details are given in the results section (4.1.3).

3.1.2.3 Experiments with AVR Pebble Graphite

The 2 samples for the KüFa measuring ~1cm diameter by 4mm thick (see section 2.3.1 and photos 2.3.6 & 2.3.7) were from each end of a carrot sample of the EU1bis/3 AVR irradiated pebble. These were composed of the outer pyrolytic graphite shell of the pebble (Carbo 1 and Carbo 2). The samples were brought into the glove box at the hot cells, were the samples could be held and a powder sample from each scraped off with a spatula for the Knudsen cell. The two samples of powder were placed in separate small aluminium containers for removal and transfer to the Knudsen cell glove box in another laboratory. One of the samples (Carbo 2) is still enclosed in the drill bit and from the higher activity level appears to have more fuel attached to it. It was also very difficult to scrape off a sample and needed to be drilled out. The Carbo 1 sample appeared to be the better, (purer) sample therefore, it was decided to take this sample first. As the prior gamma spectroscopy showed the presence of Cs isotopes, the Knudsen cell testing would also look at the heavier isotopes to monitor the fission product caesium behaviour as well as checking the lighter isotopes for indications of C-14 behaviour. The powder sample of Carbo 1-K-A was placed in a Knudsen cell and vacuumed down overnight before commencing the temperature ramp to 2700K at a steady rate. More details are given in the results under section 4.1.2.

3.2 Cold Finger Facility (KUEFA) at ITU

3.2.1 Introduction

The performance of high-temperature reactors (HTRs) under accident conditions depends to a large extent on the quality of the fuel elements. Inside the graphite matrix of HTR fuel elements, fissile material is contained in the form of thousands of small spherical fuel particles enclosed in several coating layers (≈1 mm particle diameter). Modern HTR fuel contains TRISO (tri-structural isotropic) coated particles (CPs) covered with porous carbon buffer, an inner layer of pyrolytic carbon, a layer of ceramic silicon carbide and finally an outer pyrolytic carbon layer. Together, the coatings provide a barrier against the release of fission products both in normal operation and under off-normal conditions. In order to provide robust data for reactor design and licensing, the performance of HTR fuel elements must be tested experimentally. For this purpose, irradiated fuel is subjected to conditions that simulate a depressurized loss of forced circulation (D-LOFC) accident (see, for instance, [8]).

In this reference scenario, all active heat sinks are removed and decay heat is carried away from the core only by means of natural heat transfer mechanisms (convection, conduction and

radiation). Both single Coated Particles (CPs) and entire fuel elements can be studied. In the latter case, a large number of particles is effectively investigated at the same time, providing a result with high statistical relevance. Some 25 years ago, a method to expose a spherical HTR fuel element to a simulated D-LOFC accident and to simultaneously collect all released fission products was developed at Kernforschungsanlage Jülich (KFA). Today, an improved successor device is operational at the Institute for Transuranium Elements (ITU) in Karlsruhe.

The Küfa (an abbreviation of the German "Kühlfingeranlage") is an experimental apparatus in which spherical HTR fuel elements can be heated to up to 1800°C at ambient pressure in a helium atmosphere while the release of fission gases and volatile fission products is measured. The original device was taken into operation at KFA Jülich in 1984 [9]. When the German HTR program was ended, the Küfa at KFA was decommissioned. In the framework of the European HTR-F project, parts of the Küfa as well as drawings and technical documents were transferred to ITU in 2001 [10]. The new Küfa was taken into operation at ITU's Hot Cells unit in 2005 [11]. Since then, it has been used to perform simulated accident testing on eight spherical fuel elements. With the new device it is possible to simulate heat-up accidents up to 1800°C. The ITU Küfa is currently the only device worldwide for the accident testing of entire irradiated HTR fuel pebbles. With a detection threshold of $\approx 5\times10^{3}$ Bq for ^{137}Cs, the fractional release from fuel elements irradiated to a burnup of about 10% can be determined with a relative precision of about 10^{-7}.

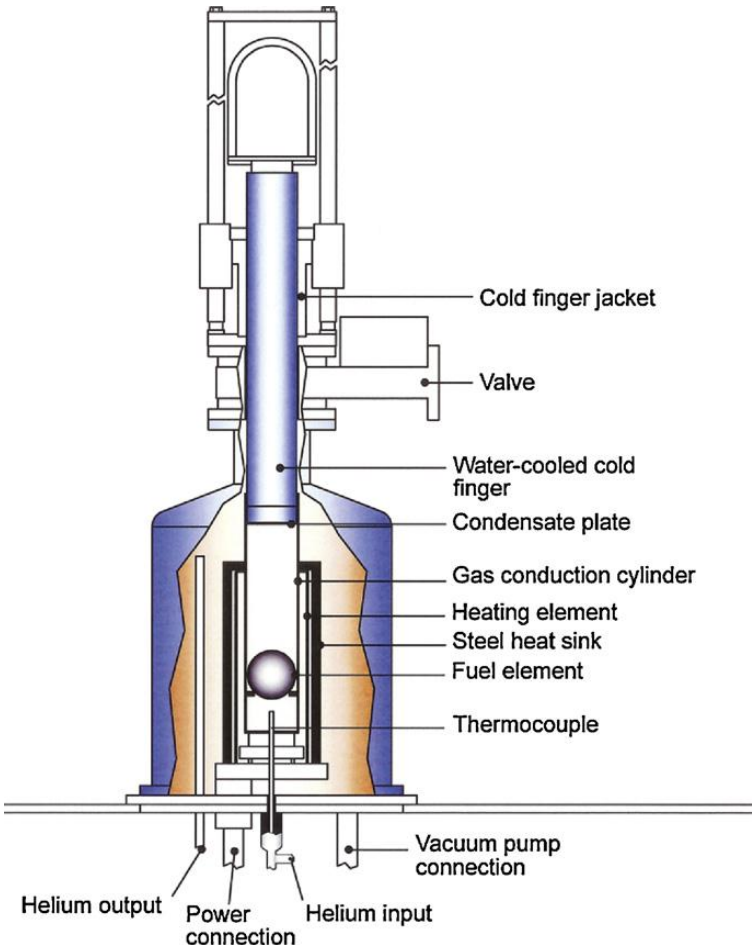

Fig 3.2.1 Schematic overview of the Küfa device at JRC-ITU

3.2.2 Experimental setup of KüFa facility

The experimental setup of the Küfa device has been described in detail in two recent articles. [49,50] In the following paragraphs, its main features will be briefly summarized. An overview sketch of the Küfa is shown in Fig. 3.2.1. Its main components are a bell-shaped outer stainless-steel vessel, a gas conduction cylinder encompassed by a heating element, and a mobile cold finger. The heater is mounted in a water-cooled copper block and surrounded by heat shields. In order to minimize the absorption of fission products in the furnace, the Küfa was designed as a metallic resistive furnace. A high-current transformer installed behind the hot cell delivers the necessary current. All high-temperature parts of the Küfa consist of tantalum because this material is the least prone to carbonization at the contact point with the fuel element. The fuel element is placed in a three-point bearing on the axis of the gas conduction cylinder, about a third of the way up the length of the heating element. A thermocouple measures the temperature about 3 mm below the fuel element and enables the regulation of the furnace power. The furnace temperature as well as all operating processes and parameters are centrally controlled by a programmable logic controller and an associated computer program. All operating parameters are collected and recorded. At the lower end of the cold finger, facing the fuel element, an exchangeable stainless-steel plate is positioned. Thanks to efficient water cooling, the surface temperature of the plate itself is kept at less than 100 °C even at maximum furnace temperatures. In this way, volatile fission products such as ^{137}Cs and ^{110}Agm plate out on the condensate plate with high efficiency. The cold finger can be pulled up through a system of locks containing a water-cooled gate valve, and the condensate plate can be exchanged semi-automatically using a manipulator. The used plates are then transported to a laboratory with low radiation background, where a gamma spectrum is recorded with a high-purity germanium detector to quantify the gamma-emitting isotopes. [50] The calibration procedures for the cold finger and the cold trap are described in detail in [50]. The cold finger efficiency was determined as 70%.

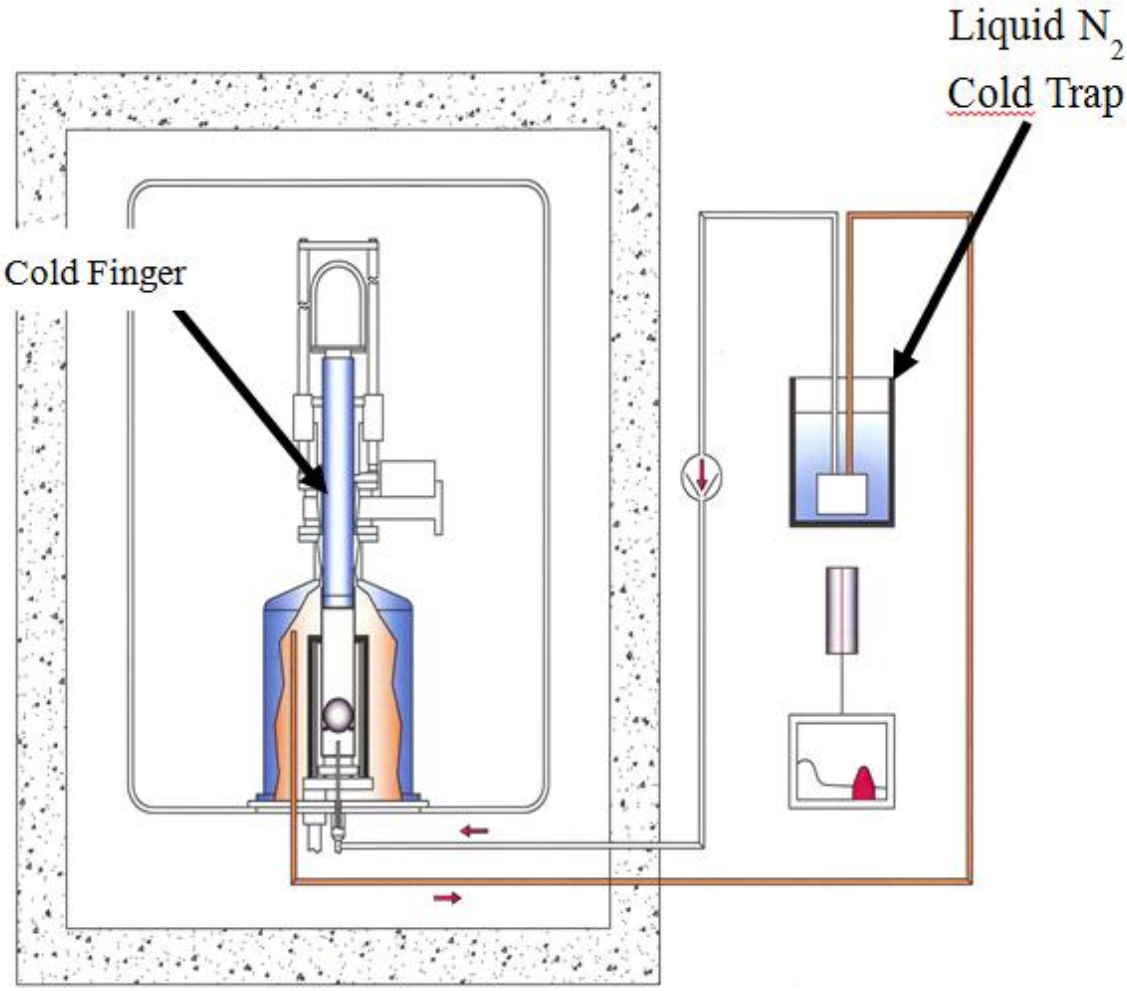

Fig 3.2.2: Diagram of the Küfa device along with the cold trap for collecting & measuring the released fission gases by gamma-spectroscopy.

During the experiment the device is flushed with helium. The helium enters the gas conduction cylinder below the fuel element, flows around it, and disperses in the bell. From there it is evacuated by a membrane pump and reaches an activated-carbon cold trap cooled with liquid nitrogen. Fission gases condense on the activated carbon and their activity can be measured by a sodium iodide gamma detector mounted below the cold trap (Stradal, 1970) – see Fig 3.2.2 For the Carbowaste project the two pebble samples (see Figure 2.3.4 in section 2.3.5 for sample description) will be annealed at approximately 1200 to 1500°C under recirculating He gas for 18h in order to determine the effect of this thermal treatment on the C-14 content. The C-14 content will be determined by Knudsen cell mass spectroscopy of small sub-samples of this material (some mg) taken before and after the annealing in the KüFa facility. As the samples are only 1cm diameter by 4mm thickness carrots extracted from the sample then they will be placed in a dummy graphite cell with a suitable aperture in order to snugly fit the samples into the pebble. This will enable the sample to be handled as a pebble and placed in the correct position in the KüFa facility for annealing. The samples were also analysed by gamma spectroscopy.

3.2.2.1 HFR irradiation

In the irradiation experiment HFR-EU1bis, five HTR fuel elements of Nukem type GLE-4.2 were irradiated at the HFR in Petten, Netherlands. The main pre-irradiation properties of the fuel elements are listed in Table 3.2.1 (standard uncertainty is given in parentheses).

Fuel element type: GLE-4.2	Kernel composition: UO_2
Graphite type: A3-3	Enrichment (U-235): 16.67%
Number of coated part. in FE: 9560	Kernel diameter: 502.2(2.0) µm
Heavy metal mass (entire FE): 6 g	Kernel density: 10.86 g cm^{-3}
Free U fraction in the matrix: 7.8×10^{-6}	
Buffer layer thickness: 92(13) µm	Buffer layer density: 1.01 g cm^{-3}
Inner PyC layer thickness: 40.6(4.1) µm	Inner PyC layer density: 1.87 g cm^{-3}
SiC layer thickness: 35.9(2.2) µm	SiC layer density: 3.20 g cm^{-3}
Outer PyC layer thickness: 39.6(3.6) µm	Outer PyC layer density: 1.87 g cm^{-3}

Table 3.2.1: General characteristics of fuel element (FE) HFR-EU1bis/3

The aim of the experiment was to investigate the potential for further improvements of HTR fuel technology based on TRISO coated particle fuel. In particular, the fuel element behaviour under VHTR conditions at increased temperature as well as increased and accelerated burn-up and increased fast neutron flux was studied [2]. After irradiation, four of the five fuel elements were transferred to ITU for Küfa accident testing and post-irradiation examination in the Hot Cells unit. One fuel element (HFR-EU1bis/2) remained in Petten and was examined in the hot cells of the Nuclear Research and Consultancy Group (NRG) [3].
After having been heated in a Küfa accident simulation up to a temperature of 1600°C, a sample from fuel element HFR-EU1bis/3 was examined with a scanning electron microscope (SEM).
A further sample was taken for the CARBOWASTE project from the outer pyrolytic graphite layer of the pebble to examine the C-14 content and its susceptibility to removal and the possible use of heating for decontamination of irradiated graphite. Details of the irradiation, the sample preparation and some ceramography of the pebble are given in the section 2.3.1.

3.2.2.2 Irradiation campaign HFR-EU1bis

During the HFR-EU1bis irradiation, the five fuel elements were irradiated for 10 cycles and a total of 249 equivalent full power days (efpd). The central temperature of the fuel elements was set to 1250°C during the burn-up cycles, except for a brief temperature excursion due to an operator error involving the gas mixing system [5]. The target burn-up was 15.4% FIMA; however, only 11.07% FIMA was actually achieved in the fuel element with the highest burn-up. The acceleration factor (defined as the reduction in time required to reach the target neutron flux, as compared with irradiation in an HTR reactor [6]) was supposed to be 7.5, whereas a value of about 5.4 was finally reached in the element with the highest burn-up.

All five fuel elements were stacked in a single irradiation rig. During the irradiation experiment, gas samples from the rig were taken about once per week and analysed by gamma spectroscopy in order to measure the fission gas release and detect potential fractured particles. Fuel element HFR-EU1bis/3 was irradiated in a central irradiation position. It reached a burn-up of 11.07% FIMA and received a fast neutron fluence of 2.86×1021 cm^{-2}. Together with pebble HFR-EU1bis/4, this fuel element had the highest burn-up of all HFR-EU1bis fuel elements. Table 3.2.2 summarizes the parameters of the irradiation campaign [2].

Beginning of irradiation:	2004-09-09		End of irradiation:	2005-10-18
Irradiation duration:	249 efpd		Irradiation temperature:	≈ 1250°C
Fractional fission gas release by end of irradiation (R/B)*				
Kr-85m	Kr-87	Kr-88	Xe-135	Xe-133
3.8×10^{-6}	2.8×10^{-6}	3.6×10^{-6}	3.6×10^{-6}	8.0×10^{-6}

* release (R) to birth (B) ratio of the nuclide

Table 3.2.2: Parameters of the HFR-EU1bis irradiation campaign

4. Experimental Results

4.1 Knudsen Cell at ITU

4.1.1 Results for Merlin graphite

Figs. 4.1.1 to 4.1.4 show the mass spectrometer spectra obtained during the Knudsen tests for low, intermediate and high mass ranges covering the mass of the nuclides of interest. No detectable release of these nuclides was measured. In fig 4.1.2 the dark blue trace is for (molecular) hydrogen while the lilac traces are for tritium and the yellow for helium. The tritium traces lie just below the expected value of natural deuterium (light blue trace). Any tritium releases were below the limits of detection at 0,01% of the H_2 concentration and clearly indicate that the Merlin i-graphite sample is not active enough to allow quantitative measurements using the Knudsen cell apparatus.

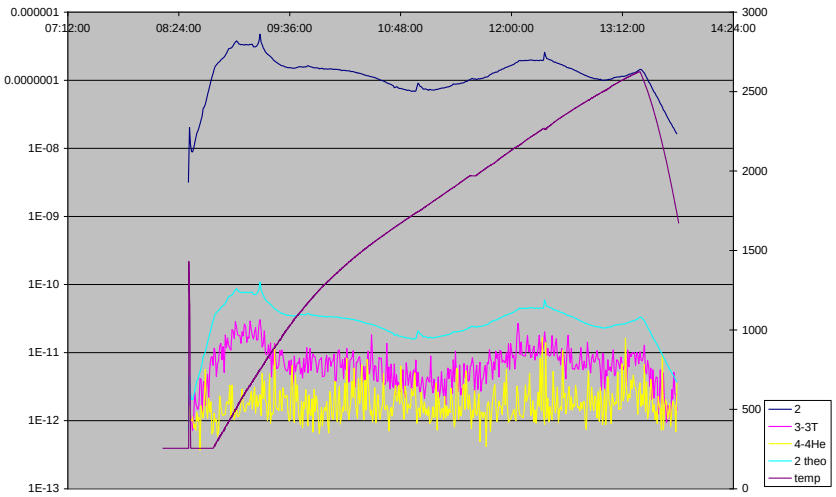

Figure 4.1.1: Knudsen cell results. Mass spectrometer signal as a function of time and temperature for tritium and helium. No major release was detectable.

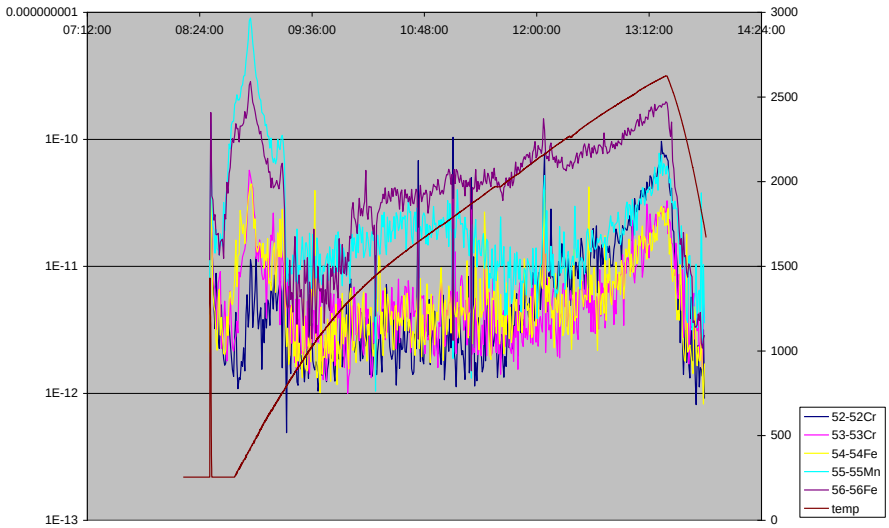

Figure 4.1.2: Knudsen cell results. Mass spectrometer signal as a function of time and temperature for intermediate mass range. No major release traceable to ^{36}Cl was detectable.

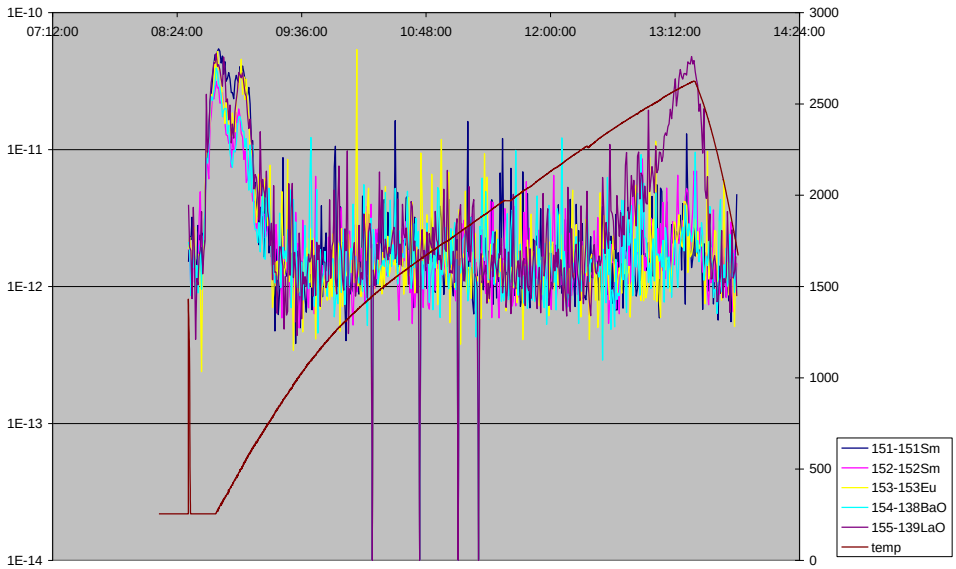

Figure 4.1.3: Knudsen cell results. Mass spectrometer signal as a function of time and temperature for high mass range. No major release was detectable.

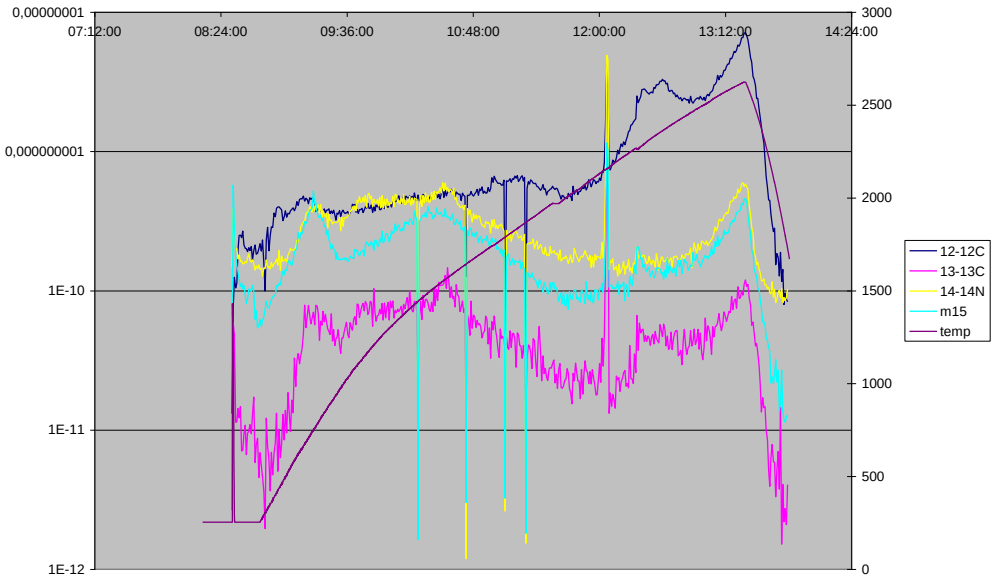

Figure 4.1.4: Knudsen cell results. Mass spectrometer signal as a function of time and temperature for carbon & nitrogen.

It can also be seen that there was a small difference between the carbon isotopes (C-13 & C-12) in their behaviour: between 700 K and 1600 K the relative releases of C-13 to C-12 is noticeably (C-13/C-12 is 0,16 to 0,2) higher than below 700 K or above 1600 K (C-13/C-12 is 0,1 to 0,02). The normal C-13 content is about 1% of C-12. It is not possible to divide the mass 14 signal between ^{14}C & traces of ^{14}N however this signal shows the same behaviour. This points to a selective release for these isotopes and suggests that the ^{13}C and ^{14}C (& ^{14}N traces) are not in an equivalent position compared to the ^{12}C matrix, but more likely displaced in the graphite lattice and/or at defect sites that are more reactive.

4.1.2 Results for AVR pyrolytic carbon sample

The AVR pyrolytic sample was tested along with a blank run using an empty Knudsen cell. The AVR Carbowaste 1-KCA sample was 86.9mg weight and had a dose rate on contact of approx. 100µSv.h^{-1}; it was loaded into the Knudsen cell along with a Ag (1.78mg) as reference. The blank Knudsen cell was a new, previously unused, W cell and so the impurities observed would originate predominantly from the vacuum and pumping lines of the system. The new, empty Knudsen cell was heated upto 2425K at a slow steady rate (~20K.mn-1) under vacuum and then cooled relatively quickly. The results are shown in Fig. 4.1.5.

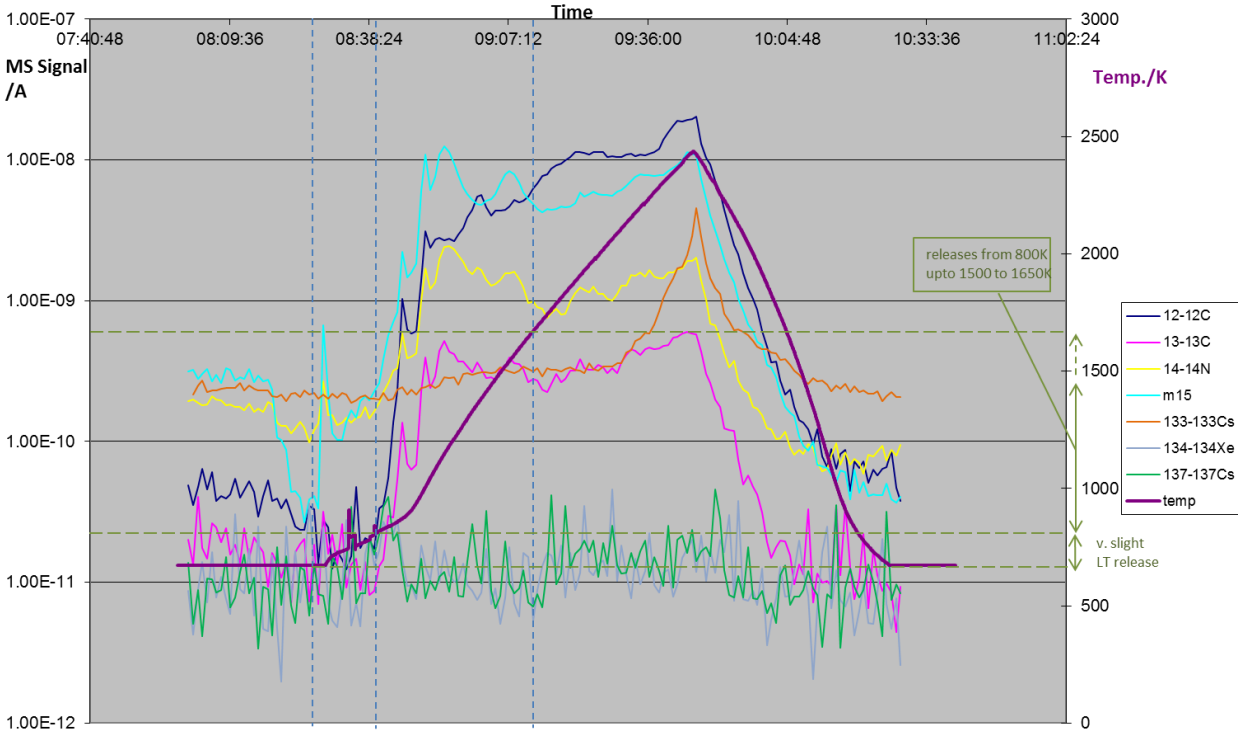

Fig. 4.1.5 Testing of an empty new Knudsen Cell as blank experiment for the AVR pyrolytic graphite sample

The sample gives signals up to 10^{-8} amp. The main signals displayed are from 12 (C-12), 14 (N) and also from Cs-133 which had been used in a previous experiment and so gave an indication of the 'memory effects' that can occur in the facility. Mass Cs-137 is also given for comparison: it is at background noise levels as is the trace of 134 (Xe-134). Mass 16 (O) and particularly 18 (water) – not shown- gave very high signals, particularly during the initial vacuuming down and the start of heating and were indicates of condensate in the system and on the new Knudsen cell. The first heating also causes the desorption of most gaseous species in a sharp initial peak, but the first releases start after 800K and here we see that 12 (C-12) starts as well as 14 (N-14). The various releases continue in stages until approx. 1650K, whereafter it remains relatively static. The only exception is the Cs-133 which is at a low steady level until about 200K and then there is a peak of release the Knudsen cell reaches its maximum temperature of 2425K. As this Cs-133 was present in a previous test sample ,then it can be assumed that this due to condensation of the Cs in adjacent parts of the metallic surfaces adjacent to the cell or in the vacuum system and that it revolatilises as these surfaces reach a higher temperature (>500°C) and appear in the analysis.
The Knudsen Cell of the AVR pyrolytic graphite sample is shown in Fig. 4.2.9.

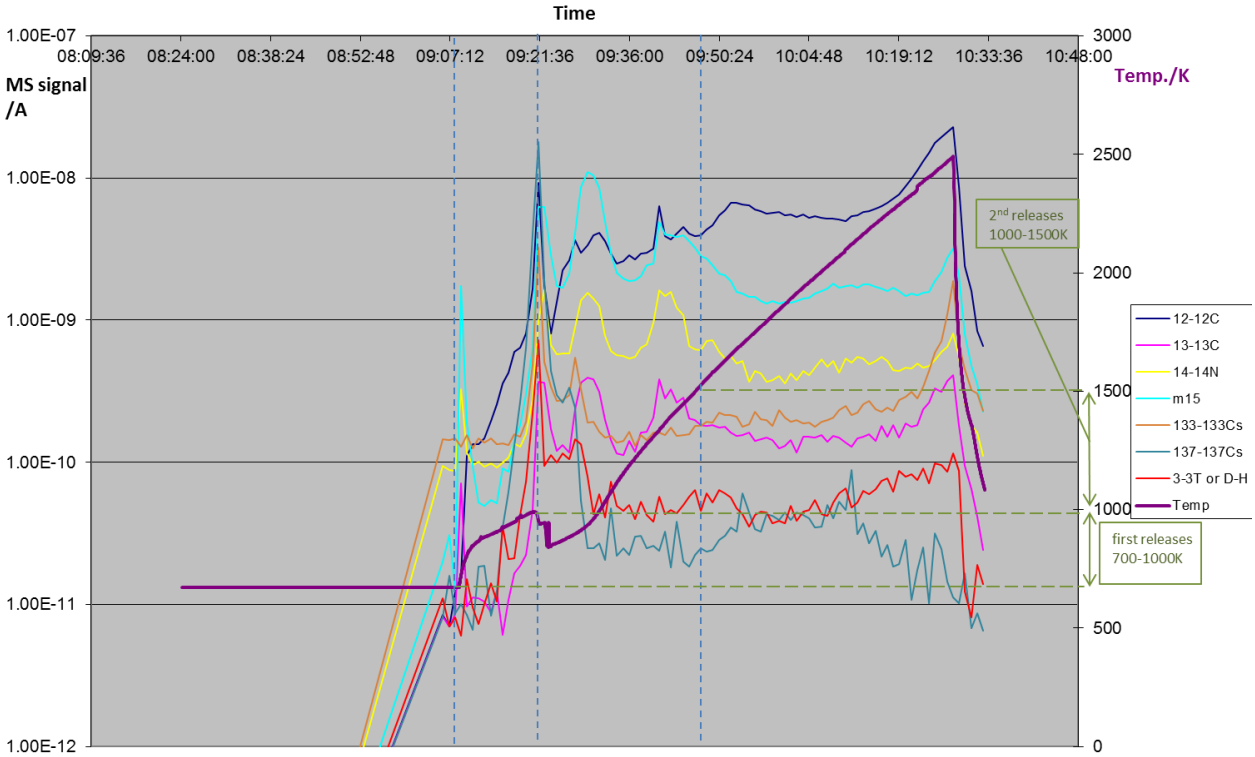

Fig. 4.1.6: Results of the powder sample taken from the carrot sample from the outer pyrolytic graphite layer of the AVR pebble.

The results are shown for masses 3 (T or D-H), 12 (C-12), 13 (C-13) and 14 (N-14), and 15 (this is thought to be an organic fragment from the pumping oils (CH_3-) rather than any N-15 (which would be about 300x weaker than the N-14 signal if natural isotopic ratios are expected). In addition masses 133 (Cs-133) and 137 (Cs-137) are also plotted. The heating was actually interrupted a short while after starting when it had reached nearly 1000K and dropped to about 840K, it then resumed the heating at a steady rate. This first heating resulted in a sharp peak of releases at just under 1000K. In the subsequent heating ramp from 840K there were similar releases at the same temperature range (~1000K) and with a slight release at 1300 to 1400K but both were much slower. Thereafter the releases were very static until the very highest temperatures (2400-2500K) when an acceleration of the releases was observed in 12 (C-12) 13 (C-13). This acceleration at the final temperature range could be due to the graphite matrix volatilisation. Cs-133 traces remaining from the previous tests were also visible (especially the releases above 2400K). By contrast the Cs-137 that is known to be in the sample (and more importantly, not in the prior blank test) gave a very sharp peak in the initial ramp to 1000K, along with the C-12 and, to a lesser extent, C-13. Mass 3 which will be predominantly D-H rather than T also shows the very sharp release at around 1000K (including a small secondary release on reheating to 1000K), but negligible releases later.

Apart from the Cs-137, very little can be said with certainty about the origin of the signals given the level of impurities present and the small sample; but considerable volatilisation appears to occur at the 1000K level. At this point the signals of the Cs-137, D-H/T, C-12,13 and N-14 peak sharply reaching about $1.E^{-8}$amps compared to only $1.E^{-9}$ amps (for Cs—137 only $1.E^{-11}$amps) in the blank test. This would suggest that if an irradiated graphite sample was heat-treated under vacuum then it is clear that volatilisation of Cs-137 occurs in this temperature range. It seems likely that the release of other activation products such as C-14 and T that are not likely to sit in the i-graphite lattice could also occur at the same time. The later slower

releases above 1000K, when compared with the blank experiment, seem to be highly likely to be due to impurities in the adjacent system volatilising under various conditions and temperatures as the furnace heats up.
In order to check this point about impurity effects, a plot of the 14 amu signal versus vacuum level has been made in Figure 4.1.7 indicating good match between vacuum increase and the Knudsen cell mass spectroscopy peaks just after the temperature drop in the middle of the ramp. This comparison supports the fact that the 14 amu signal measured above the sample has a very large background nature and gives little indication with respect to the sample behaviour in this mass range during heating.

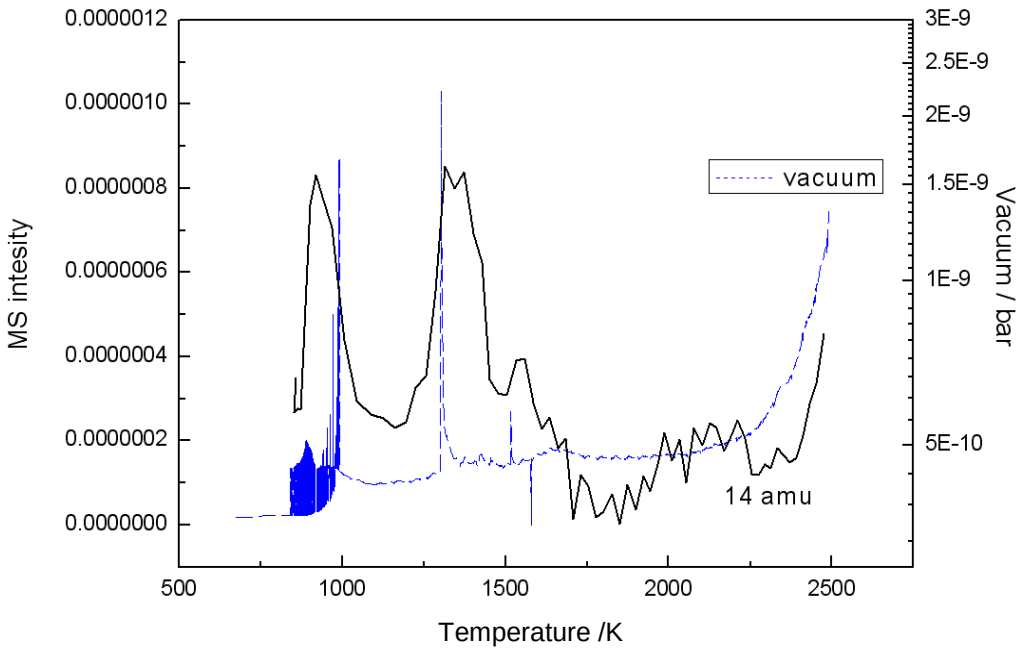

Figure 4.1.7: A comparison of a vacuum signal with the 14 amu signal during the heating of pyrolytic carbon sample ('Carbo-1-KC-A').

4.1.3 Results for Latina graphite

A sample of the most active of the LATINA Graphite samples (04F04A1/C1 with 1.6µSv.h^{-1} contact dose rate) was scraped off the main sample and placed in a separate metal container for transfer to the Knudsen Cell facility in the adjacent building (see Fig. 4.1.8). The most active sample was tested first in order to have the best chance to observe the radioactive isotopes of interest.

Fig. 4.1.8 Samples of the Merlin graphite arriving at ITU and being unpacked (left); on the right the C1 (highest dose rate) pellet sample having a small powder sample scraped off (~40mg) and being placed in a small aluminium container (on the right hand side) for Knudsen Cell testing.

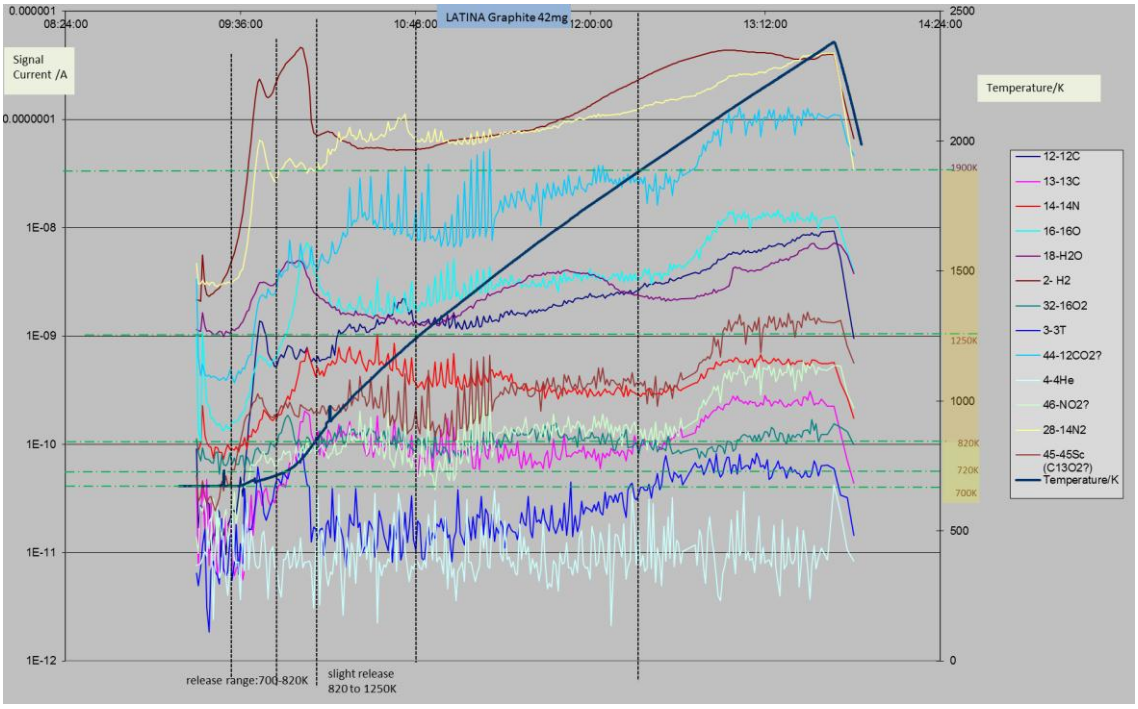

Fig. 4.1.9 Knudsen Cell Testing of the LATINA Graphite sample (C1) under vacuum upto 2380K

38.5 mg of the Latina i-graphite powder sample (with a ~2mg Ag reference material) was placed in a metallic (W) Knudsen cell. The sample was then placed under vacuum and heated at a steady slow rate to 2400K and then rapidly cooled under vacuum and the mass spectrum repeatedly taken during the entire heating period. The results are shown in the figure 4.1.9.

The graph shows the mass traces for the weights of C-12, C-13 & N-14 (the C-14 will be too low compared to the N-14 atoms to be distinguishable. Calculations based on the specific activity of the LATINA sample show that the signal to be expected from the C14 will be well below 10-12A and so well below any detection limit.
Other masses shown on the graph are: H_2-2, T-3, O-16, H2O-18, O_2-32, N_2-28, $C^{12}O_2$-44, $N^{14}O_2$-46 (?). 2 (H_2) and 28 (N_2) are the major signals followed by (44) ($C^{12}O_2$) oxygen (16) and 18 (water) and 12 (C-12). The C-13 trace is at about the expected ratio to C-12 (1%). Therefore one is dependent on general observations of the gaseous and non-volatile species behaviour to make some deductions.
The main releases are at 720-820K of gaseous species but also other species. Thus at 720K there are releases of 2 (H_2), 28(N_2), 14 (N), 16(O), 18(H_2O) 32 (O2), and 44(CO_2), but also 12(C-12), 13 (C-13). Thereafter there are broader or slight releases upto 1250K but these are either steady with temperature or are oscillating as in the 44, 45, & 46 masses. At higher temperatures 1500 to 2000K the releases are relatively constant with a slight step as temperatures go from 1900 to 2000K.These mid-range oscillations may be due to the variations in the heating or to pumping variations (see section final paragraph 4.2.1)and is probably a volatile species. 44 can be CO_2, 45 could contain $C^{13}O_2$ (expected ratio compared to $C^{12}O_2$ signal); 46 could be NO_2 with traces of $C^{14}O_2$ but it is impossible to determine this.

C-12 after the initial releases at low temperature (700-860K), has a secondary release at upto 1250K; thereafter it is very constant with rising temperature upto 2300K. This compares with the MERLIN Knudsen cell sample which went upto 2600K and in the last 200K there was a noticeable sharp increase in signal that suggested more matrix vaporisation. This was absent in the LATINA sample as the sample was not heated to high enough temperatures. The C-13 has slightly different releases from C-12 in the low temperature releases (700-820K).

With so many impurities present it is very difficult to make any concrete statements. However most releases were at low temperatures whether they were gaseous or not, but how much of this was from the samples is impossible to state. Nevertheless it suggests that heating under inert atmosphere or vacuum may detach or remove a wide range, not just gaseous, species. Given the problems in concluding the origin of the Knudsen cell signals for the most active i-graphite sample, it was decided not to continue further with other Latina samples but pass to the pyrolytic graphite sample.

4.2 Cold Finger Facility (KUEFA) at ITU

4.2.1 Gamma Spectroscopy on AVR pebble graphite

Gamma–spectroscopy was performed on the pre-test Carbowaste samples ("Carbowaste 2" and both pre-test Knudsen cell samples) using a High Purity Germanium detector & Orion MCA analyser to verify the major gamma emitting isotopes initially present in the samples.

The results are given in Fig. 5.3.5 for "Carbowaste-2", and the 2 pretest Knudsen cell samples "Carbowaste-1–KC-A" and "Carbowaste-2-KC-A". "Carbowaste 2" sample (blue trace) is clearly the most active. All show the same main peaks: Cs-134 and Cs-137 peaks along with Co-60. The analysis software also identified Eu-152, Eu-154 and Sb-125 peaks for the "Carbowaste 2" sample. This indicates detectable traces of fuel on the "Carbowaste 2" sample.

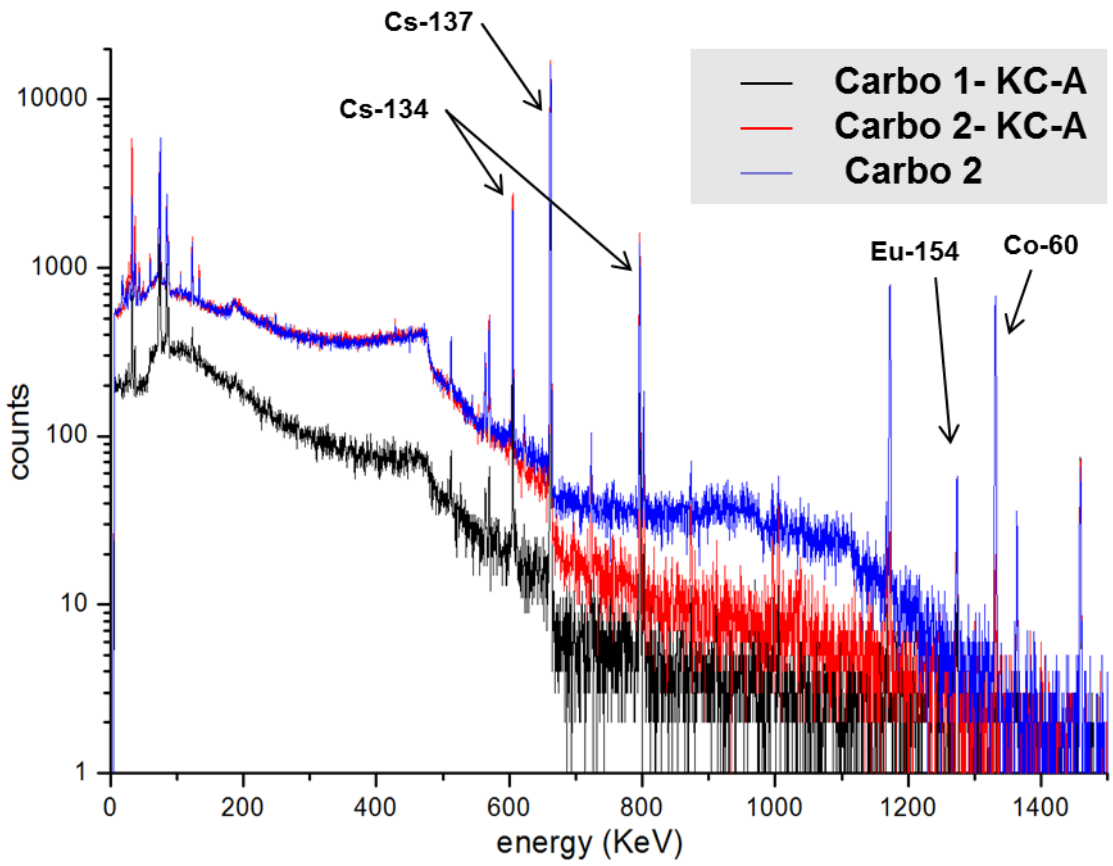

Fig 4.2.1: Gamma spectroscopy of the Carbowaste-2 sample and the 2 pre-test samples, showing the caesium-134,137 peaks and the Co-60 peaks.

Activities of the most active (Cs) isotopes of the 3 samples - as estimated from the gamma spectra - are given in table 4.2.1 below.

Activity(Bq)	Cs-134	Cs-137
CARBO 1-KC-A	7.32E+03	6.74E+04
CARBO 2-KC-A	6.99E+04	5.87E+05
CARBO 2	5.82E+04	5.45E+05

Table 4.2.1 table of estimated Cs-134 & Cs-137 activities of the 2 Knudsen cell samples and one of the KüFa samples taken from the outer shell of the AVR fuel element prior to testing.

Due to the delays and breakdown in the KüFa facility it was not possible to carry out post-heating gamma spectroscopy to determine the losses in gamma-emitting isotopes from the pyrolytic graphite. It is hoped to include these results in the report if the tests can be carried out in the near future

4.2.2 Results for AVR fuel pebble

The following irradiated graphite samples (~4mm thick) were extracted from the AVR pebble:

- "Carbowaste 1" (0.4 $mSv.h^{-1}$) – outer PyC graphite shell only.
- "Carbowaste 2" (11 $mSv.h^{-1}$) – outer Pyrolytic graphite shell + fuel traces on the inner side

These are to be firstly measured by gamma spectroscopy, and small samples extracted for Knudsen Cell (KC) testing upto 2000K or higher until total evaporation under high vacuum (samples are Carbowaste 1-KC-A & Carbowaste 2 –KC-A).
Then the samples will be reinserted into a dummy pebble and placed in the KüFA facility for heating under He flow to 1500°C for Carbowaste 1 and to 1200°C for Carbowaste 2 (Carbowaste 2 is limited in temperature because part of the hollow steel drill bit surrounds the sample – going higher than 1500°C would melt the steel).
After heating they would be extracted from the dummy pebble and a small sample scraped or drilled out of the samples (20-70 mg) in order to provide post-test samples for the Knudsen Cell (samples Carbowaste1-KC-B and Carbowaste -2-KC-B). These would then be annealed under the same conditions as previously ($\geq$2000K under vacuum). For the main part of the annealed samples, gamma spectra would be made.
It was intended that the comparison of the pre-test and post-test gamma spectra will enable the release of gamma-active isotopes to be estimated, while comparison of the Knudsen Cell spectra particularly the 14 atomic mass unit (amu) and 12 /14 amu ratios between pre-test and post –test would indicate any changes in the C-14 or contents or C-14 to C-12 ratios. Possibly using the CO^+ and $C(14)O^+$ ratios (amu: 28 & 30) or even the CO_2^+ and $C(14)O_2^+$ ratios (amu: 44 & 46) would be helpful. Analysis was also intended on the KC mass spectra of hydrogen, deuterium and hydrogen and their peak ratios in the spectra from the 2 pre-annealed Carbowaste samples and the 2 post-annealed Carbowaste samples. It was hoped that a relative reduction in the amounts of C-14 and H-3 (T) may be observed in the post-annealed HTR irradiated graphite samples.

However the final tests with the Knudsen Cell on the pyrolytic graphite showed a large level of impurities that were degassing from the various parts of the facility, such as heat shields or adjacent gas lines that are heating up more slowly than the furnace and so it was very difficult to get any firm conclusions on the source of many signals. Thus C-12 & C-13 could be identified easily but C-14 traces will be overlaid with the natural contaminant levels of nitrogen. This was confirmed in the pre-test Knudsen cell results, therefore the post-test Knudsen cell will not be carried out.
The KüFa tests have also been delayed due to repairs and up-dating of the facility, but it is hoped that the KüFa annealing tests, as described in the experimental section, can be carried out in the near future and then the post-test gamma –spectroscopy of the KüFa samples could possibly be included at a later stage in the report.

Conclusions of ITU Knudsen Cell testing

Knudsen Cell testing of the various irradiated graphite samples has been carried out.; these include the MERLIN i-graphite, LATINA i-graphite and the outer pyrolytic layer from an fuel element of the high temperature gas-cooled reactor (AVR pebble), with the aim of determining at what temperatures the T-3 and C-14 in the samples is released during thermal treatment under vacuum conditions. Samples of the Outer pyrolytic graphite were also intended to be heat treated under inert atmosphere conditions as well, however the breakdown of the facility prevented these final tests from being carried out. It is difficult to draw definite conclusions with so many impurity effects, but some observations can be made.

The analysis of the MERLIN graphite resulted in detectable deuterium releases but T (or H-3) was well below the detection limit. The C-13 signal was detectible but the C14 was swamped by the N-14 signal. Some very slight releases occurred at the temperature range of 800 to 1000K. No particular low temperature releases were observed of mass 12 (C-12); a slight acceleration of the releases at the highest temperatures which could be attributed to matrix volatilisation about 2500K.

The testing of the more active LATINA i-graphite, did result in more pronounced releases. Following the usual desorption signals when heating is started there were initial releases at 720 to 820K; often a sharper first release and second broader release. The further, broad releases from 1000 to 1250K may be impurities; the some oscillating traces in this temperature may be experimental artefacts (possibly a slight release at 1250K from C-12 could be from the sample). Thereafter it is relatively static upto the final temperature. It is virtually impossible to assign any of the traces to the sample, but the most likely volatilisation from the sample will be contained in the low temperature range of releases at 720-820K.

The sample from the pyrolytic graphite of the AVR pebble was the most difficult to interpret because of the blank Knudsen cell test indicating the level of impurities that are in the facility. However, the HTR i-graphite appeared to give some particularly fast low temperature releases at around 1000K of most masses: for example 2(H_2) 3 (D-H), 12 (C-12), 13 (C-13) and 14 (N-14). The repeated slower releases will be dominated by impurity effects. From the H_2 and D-H signals one would presume that tritium would behave similarly. The C-12, 13 signals will be difficult to use in predicting the C-14 behaviour as it is expected the C-14 (as activation product of C-13) will not lie in the lattice but more likely to be in an interstitial or vacancy position. Here the mass 14 (N-14) will be perhaps more useful as the C-14 is more efficiently formed by (n,p) reaction with N-14 than by C-13 neutron capture by a factor of nearly 10^5x. However it is clearly seen that the 14 mass (N-14) also had a large low temperature release and although a large part of the signal may come from N that is not in the sample but as impurity in the system at 1170 to 1270K (see Fig.4.1.7), it does suggest that N, bound at a surface, may be released at relatively low temperatures.
Cs -137 which is clearly from the sample also was released very sharply at this temperature and in a larger quantity than the Cs-133 which is seen from the blank test to be a memory effect from earlier testing (continuing across both the blank and real test). This result also supports the idea that other adsorbed elements or activation/fission products not in the graphite lattice may also volatilise in the same temperature range.

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