



Institut für Sicherheitsforschung und Reaktortechnik

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conditions and thermal treatment***

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Berichte des Forschungszentrums Jülich ; 4166

ISSN 0944-2952

Institut für Sicherheitsforschung und Reaktortechnik Jül-4166

D 82 (Diss., Aachen, RWTH, 2004)

Zu beziehen durch: Forschungszentrum Jülich GmbH · Zentralbibliothek

D-52425 Jülich · Bundesrepublik Deutschland

☎ 02461 61-5220 · Telefax: 02461 61-6103 · e-mail: zb-publikation@fz-juelich.de

Graphite as radioactive waste: corrosion behaviour under final repository conditions and thermal treatment

The present work deals with radioactive graphite management. Two different aspects were examined:

1. The corrosion behaviour of graphite under final repository conditions
2. The decontamination of graphite by thermal treatment

Spent fuel from the German AVR and THTR high-temperature reactors is envisaged for direct disposal in a final repository. In this respect, corrosion of the graphite matrix of the spherical fuel elements and pyrocarbon coatings from coated fuel particles is a very important aspect for predicting the long-term behaviour of the radioactive waste.

The graphite materials to be examined were isolated from unirradiated fuel elements, and their corrosion was investigated in different aqueous phases. The experiments were performed in deionised water, MgCl_2 -rich (brine-2) and NaCl -rich (brine-3) solutions at 90°C under argon, oxygen and air atmosphere. In order to investigate the influence of aqueous phase radiolysis, further experiments were performed in the presence of γ -irradiation sources under argon atmosphere.

It was established that the slow corrosion of carbonaceous materials in different aquatic phases in the absence of irradiation was caused by interaction with dissolved oxygen. Corrosion rates in aqueous solutions under pure oxygen and air atmosphere decrease in the order $\text{water} > \text{brine-3} > \text{brine-2}$. Acceleration of graphite and pyrocarbon corrosion was observed in the presence of γ -irradiation in brines while the opposite influence of the aqueous phases on the corrosion rates was additionally observed. The corrosion rates of graphite and pyrocarbon in irradiated brine-2 and brine-3 in argon atmosphere were two orders of magnitude higher than in pure oxygen atmosphere without irradiation. This may be related to the formation of highly oxidising chlorine species in brines, which react with carbon materials. In pure water, radiolysis did not influence the oxidation process significantly. However, calculating the expected lifetime of the graphite matrix in the repository on the basis of the corrosion rates determined is an extremely conservative consideration since the radiation dose rates used are significantly higher than could ever occur during final disposal of high-temperature reactor fuel elements.

In the second part of the present work, thermal treatment of contaminated structural graphite from the high-temperature reactor core and thermal columns of the research reactors was investigated as a possible decontamination process. The main problem associated with direct disposal of contaminated graphite is its large volume. Reprocessing of the graphite based on graphite gasification offers the opportunity to separate the radionuclides from the main graphite mass, which could then be reused or disposed conventionally.

The experiments were performed in an argon flow and steam in the temperature range of $870 - 1060^\circ\text{C}$. Comparison of the release rate ratios of the volatilised radionuclides ^{14}C and ^3H with the release of ^{12}C showed that under all experimental conditions tritium and ^{14}C were released faster than the graphite sample was oxidised.

The maximum value of the release rate ratio was obtained for tritium in experiments with argon atmosphere at 1060°C .

It was shown that ^{14}C could be separated from the main graphite mass with a $^{14}\text{C}/^{12}\text{C}$ enrichment factor of about 20. However, the total fractional release was not sufficient for a pilot scale process under these conditions. The fractional release of ^{14}C can be increased by addition of water steam, but in this case the enrichment factor drops below 5. In general, this

separation of carbon isotopes is only possible because ^{14}C is mainly located near the grain boundary surfaces and its concentration profile decreases with depth inside the graphite grains.

The radionuclides ^{60}Co , $^{154,155}\text{Eu}$, $^{134,137}\text{Cs}$ and ^{133}Ba present in contaminated graphite mainly remained in the ceramic reaction boat in contrast to the volatile Cs.

By optimising the process parameters this decontamination process may be developed further into a pilot scale technology for graphite purification with fractional reduction of the ^{14}C inventory.

Graphit als radioaktiver Abfall: Korrosionsverhalten unter Endlagerbedingungen und thermische Behandlung

Diese Arbeit steht im Zusammenhang mit der Entsorgung von radioaktivem Graphit. Dabei wurden zwei verschiedene Aspekte betrachtet:

1. Das Korrosionsverhalten von Graphit unter Endlagerbedingungen
2. Die Dekontamination von Graphit durch eine thermische Behandlung

Da die beim Betrieb der deutschen Hochtemperaturreaktoren AVR und THTR angefallenen Brennelemente direkt endgelagert werden sollen, ist die Korrosion der Graphit-Matrix der kugelförmigen Brennelemente und Pyrokohlenstoffschichten der Brennstoffpartikel von großer Bedeutung für die Vorhersage des Langzeitverhaltens dieser Abfälle.

Die Graphitmaterialien wurden aus unbestrahlten Brennelementen isoliert und deren Korrosion in verschiedenen wässrigen Phasen untersucht. Die Versuche wurden in destilliertem Wasser sowie in MgCl_2 -reichen (Lauge-2) und NaCl -reichen (Lauge-3) Lösungen bei 90°C in Gegenwart von Argon, Sauerstoff und Luftatmosphäre durchgeführt. Um den Einfluss der Radiolyse der wässrigen Phase zu untersuchen, wurden weitere Experimente unter Argon-Atmosphäre mit äußerer γ -Bestrahlung durchgeführt.

Es wurde festgestellt, dass eine langsame Korrosion der kohlenstoffhaltigen Materialien in verschiedenen Lösungen ohne Bestrahlung durch die Wechselwirkung mit gelöstem Sauerstoff auftritt. Die Korrosionsraten in wässrigen Lösungen in Gegenwart einer reinen Sauerstoffatmosphäre und Luftatmosphäre nehmen in der Reihenfolge Wasser > Lauge-3 > Lauge-2 ab. Unter dem Einfluss von γ -Strahlung wurde eine beschleunigte Korrosion beobachtet, wobei zusätzlich ein entgegengesetzter Einfluss der wässrigen Phasen auf die Korrosionsraten beobachtet wurde. Die Korrosionsraten des Graphits und Pyrokohlenstoffs in bestrahlter Lauge-2 und Lauge-3 in der Argon-Atmosphäre waren zwei Größenordnungen höher als in der reinen Sauerstoff-Atmosphäre ohne Bestrahlung. Dies ist mit Bildung von reaktiven, oxidierenden Chlor-Spezies in den Salzlösungen verbunden, die dann mit Kohlenstoff-Materialien reagieren. In reinem Wasser beeinflusste die Radiolyse den Oxydationsprozess nicht signifikant. Die Berechnung der im Endlager zu erwartenden Lebensdauer der Graphitmatrix auf Grund der ermittelten Korrosionsraten ist jedoch eine extrem konservative Betrachtung, da die verwendeten Strahlungsdosisraten wesentlich höher waren, als sie bei der Endlagerung der Hochtemperaturreaktor-brennelemente jemals auftreten könnten.

Im zweiten Teil der Arbeit wurde die thermische Behandlung von kontaminiertem Strukturgraphit aus dem Core der Hochtemperaturreaktoren und thermischen Säulen aus Forschungsreaktoren als mögliches Dekontaminationsverfahren untersucht. Das mit der direkten Endlagerung des kontaminierten Graphits verbundene Hauptproblem ist sein großes Volumen. Die Aufbereitung des Graphits, basierend auf der Graphit-Vergasung, bietet die Möglichkeit, die Radionuklide vom inaktiven Kohlenstoff zu trennen, der dann weiter verwendet oder konventionell entsorgt werden könnte.

Die Untersuchungen wurden in Argon- und Wasserdampf-Atmosphäre in einem Temperaturbereich von $870 - 1060^\circ\text{C}$ durchgeführt. Der Vergleich der Verhältnisse der Freisetzungsraten von ^{14}C und ^3H zu ^{12}C zeigte, dass bei allen experimentellen Bedingungen Tritium und ^{14}C schneller freigesetzt wurden, als die Graphitprobe oxydiert wurde.

Für Tritium wurde ein maximales Verhältnis der Freisetzungsraten in Argon-Atmosphäre bei 1060°C erzielt.

Des weiteren konnte gezeigt werden, dass ^{14}C mit Anreicherungsfaktoren von bis zu 20 gegenüber ^{12}C von der Hauptmenge des Graphits abgetrennt werden kann. Jedoch ist der Gesamtumsatz unter diesen Bedingungen nicht ausreichend für einen technischen Prozess. Durch Zusatz von Wasserdampf kann der Gesamtumsatz erhöht werden, wobei die Anreicherungsfaktoren jedoch auf unter 5 absinken. Generell ist diese Trennung der Kohlenstoffisotope nur deshalb möglich, weil sich das ^{14}C hauptsächlich nahe der Korngrenzenoberflächen befindet und sein Konzentrationsprofil mit der Tiefe innerhalb der Graphitkörner abnimmt.

Die Radionuklide ^{60}Co , $^{154,155}\text{Eu}$, $^{134,137}\text{Cs}$ und ^{133}Ba , die im radioaktiven Graphit gegenwärtig sind, verblieben während der thermischen Behandlung, mit Ausnahme des flüchtigeren Cs, hauptsächlich in dem verwendeten Keramikreaktionsgefäß.

Durch eine weitere Optimierung der Verfahrensparameter könnte diese Methode zu einem technischem Verfahren zur Reinigung von Graphit mit einer partiellen Reduktion des ^{14}C -Gehalts weiter entwickelt werden.

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A. Introduction and objectives

Graphite has been widely used as a moderator, reflector and fuel matrix in various types of nuclear reactors. At the end of the reactor's life activated graphite and carbon installations are radioactive waste, which requires a special waste management strategy.

In Germany two high temperature gas-cooled and graphite moderated reactors were developed: the 15 MWe AVR (Arbeitsgemeinschaft Versuchsreaktor) plant and the 300 MWe Thorium High Temperature Reactor (THTR 300). At the end of 1988 the reactors were shut down (AVR after 21 years of operating and THTR after 3 years of operating). About 300000 AVR and 620 000 THTR fuel elements were irradiated during the operational time. The fuel of this reactor type consists of small uranium/thorium oxide spherical particles of about 0.5 mm in size. The fuel particles are coated with pyrocarbon coating (BISO) or a combination of pyrocarbon and silicon carbide coatings (TRISO) up to 1 mm in total diameter. About 20000 coated particles are embedded in a graphite matrix of spherical form about 6 cm in diameter.

The proposed solution for HTR spent fuel management in Germany is storage in deep geological formations without reprocessing. Three types of rocks are considered as host units: granite, clay and salt domes. The long term safety depends on the integrity of the multibarrier system of the waste package [1] and the integrity of spent fuel element itself.

As an accident scenario ground water ingress into the repository and its interaction with the protective barriers of graphite and the pyrocarbon coatings should be taken into account. The first experiments with HTR spent fuel elements demonstrated that extremely low amounts of radionuclides were released from the graphite matrix and coated particles [2]. However, the chemical impact of aqueous phases on graphite matrix and pyrocarbon coatings in the long term is unknown. In this respect, the investigation of graphite and pyrocarbon behaviour in repository relevant conditions is important.

The other problem is associated with reflector graphite, which becomes a radioactive waste at the end of reactor life. Direct disposal in deep geological formations is one of the most probable ways of radioactive graphite management. However, the large volume of contaminated graphite significantly reduces the cost efficiency of this management route. For example, in the case of AVR decommissioning 67 Mg of reflector graphite and 158 Mg of carbon isolation represent a great volume of low and medium active radioactive waste. This graphite contains significant quantities of radionuclides from the neutron activation of impurities and contamination with fission products. Reprocessing of the graphite offers the opportunity to separate the majority of the short-lived isotopes from the graphite. Thereafter only a small active residue fraction has to be disposed and the main mass of graphite can be reused.

The existing purification procedure is based on graphite gasification. This procedure allows non-volatile and volatile radionuclides to be separated by chemical methods. The CO₂ formed can be released to the atmosphere or precipitated as carbonates. Chemical methods are not capable of separating the carbon isotopes: long-lived radioactive ¹⁴C and non-radioactive ¹²C. In principle, the off-gases from incineration can be fractionated in order to recover ¹⁴C by isotope separation. However, the development of a more simple method for graphite purification from ¹⁴C would give an additional economical benefit.

The main objectives of the present work were:

- Determination of the corrosion rates and investigation of the graphite matrix and pyrocarbon coating behaviour in different aquatic phases.

- Investigation of the influence of high-temperature treatment on the release of radioactive carbon and other radionuclides from contaminated graphite.

B. Statement of problem

B.1. Graphite in nuclear technology

The properties of graphite make it suitable for many nuclear applications. By far the greatest use has been as a moderator and reflector, because nuclear graphite has an absorption cross section for thermal neutrons as low as 3.5 to 3.8 mb. Furthermore, graphite is strong enough to serve as a structural component, eliminating the necessity of using metals with higher cross sections.

The high-temperature strength, stability, and thermal conductivity of graphite make it good for use in high-temperature reactors as a matrix material for ceramic fuels such as the uranium oxides and carbides.

In the reactor core, boronated graphite is sometimes used as a high-temperature control-rod material. Designs for gas-cooled reactors employ graphite sleeves that support the fuel elements and channel the coolant. Also it is useful as a container for reactor irradiation experiments.

B.1.1. Graphite structure

Pure graphite is one of the most chemically inert materials. It is resistant to most acids, alkalis and corrosive gases. The crystallographic structure has a considerable influence on the chemical reactivity of graphite.

The basis of the crystal structure of graphite is the graphene plane of the carbon layer plane, i.e. an extended hexagonal array of carbon atoms with sp^2 σ bonding and delocalised π bonding. The most common crystal form of graphite is hexagonal and consists of a stack of layer planes in the stacking sequence ABABAB

The rhombohedral form of graphite with a stacking sequence ABCABC is a minor component of well-crystallised graphite. The theoretical density of both forms of graphite is 2.26 g/cm^3 ; the in-plane C–C distance is 0.142 nm and the interlayer distance 0.335 nm. Such a difference results from different types of chemical bonding. The usual assumption is that interlayer potentials are of van der Waals type. The bond strength within the layer planes is approximately 150 kcal/(gram atom), whereas the interlayer binding energy is estimated to be 1.3 kcal/(gram atom).

The structure given in Figure 1 is the perfect crystal structure of graphite. Solid carbons, in general, are less perfect. They consist of domains of carbon atoms arranged in a hexagonal pattern but these domains vary in degree of ordering and value of interlayer space. Interlayer spacing is larger than for the graphite crystal (up to 0.344 instead of 0.335 nm). The most disordered carbons have a so-called “turbostratic” structure with carbon layer planes oriented randomly about the c-axis.

Pyrolytic carbon has such a structure, usually with many warped basal planes, lattice defects and crystallite imperfections.

The anisotropy of the graphite crystal leads to different physical properties and chemical reactivity in different crystallographic directions. The energy of the prismatic plane amounts to 5 J/m^2 and 0.11 J/m^2 for the basal plane, so reactions take place preferably at the edges (prismatic surface) and at defect sites.

As it was shown by Laine and co-workers [3], the different reactivity of carbon materials can be ascribed to the fact that different carbons have, initially, different amounts of active surface area. Graphite materials with large crystals and few defects have the best chemical stability.

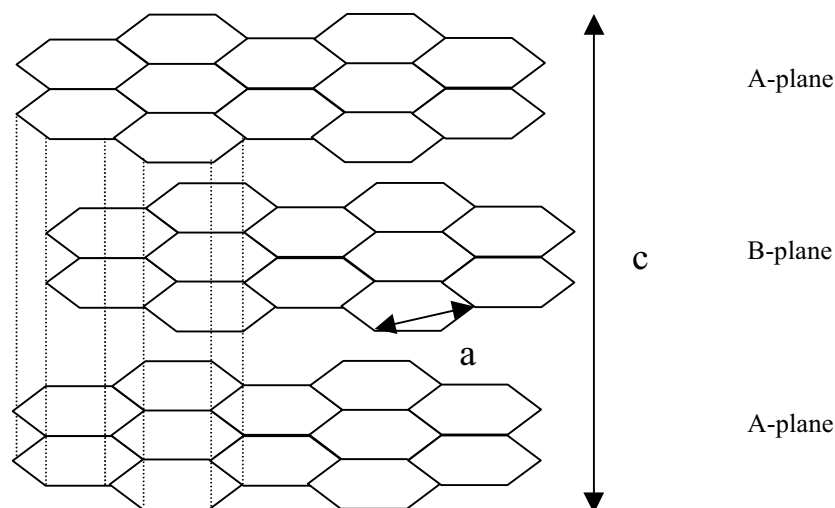


Figure 1. The crystal structure of hexagonal graphite

B.1.2. Chemical reactions of carbon

B.1.2.1. Gas-phase reactions

At room temperature graphite does not react with gases like O_2 , CO_2 , H_2O and H_2 . Above $400^\circ C$ these gases start reacting with graphite. The temperature at which reaction takes place depends on the perfection of the graphite's crystal structure.

Heterogeneous reactions involving a porous solid and a gas can be controlled by one or more of three idealised steps:

1. Mass transport of the reacting gas from gas stream to the exterior graphite surface.
2. Mass transport of the reacting gas from the exterior surface to active sites and mass transport of the products in the opposite direction.
3. Chemical reaction at the active sites.

The variation of reaction rate with temperature for gas-carbon reactions can be divided into three main zones (Figure 2).

In the low-temperature zone I, the reaction is controlled by the chemical reactivity of the solid (step 3). There will be almost no concentration gradient of reacting gases throughout the whole volume of the sample due to the low reaction rate, and this provides uniform access to the entire interior surface of the porous material. For the graphite–oxygen reaction the upper limit for temperature will be $500^\circ C$, for the graphite–water steam system $850^\circ C$ [4].

In the intermediate-temperature zone (zone II), step 2 becomes important. The diffusion of reactants in pores will influence the oxidation rate of the material. At higher temperatures the concentration gradient of the reacting gas becomes steeper within graphite and the gas concentration becomes zero at a distance R closer to the surface. The activation energy E_a amounts to $\frac{1}{2}$ of the true activation energy E_t in this zone. For the graphite–water steam

reaction this temperature region is characterised by temperatures of 850–1350°C and the graphite–oxygen reaction by 500–900°C.

In the high-temperature zone (>900°C for graphite oxygen and >1250–1400°C for graphite–water steam) – zone III – the concentration of the reacting gas is low at the exterior of the solid and the rate is controlled by step 1. Since bulk gas-transfer processes have low activation energies, the apparent activation energy for gas–carbon reactions in zone III is low.

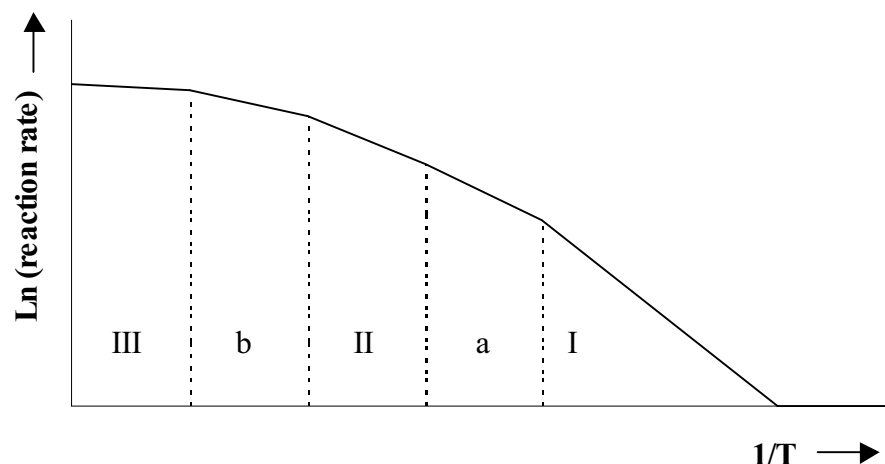


Figure 2. Ideal reaction zones in graphite: I – reaction rate is controlled by chemical reactivity of the sample; II – reaction rate is controlled by diffusion in pores; III – reaction rate is controlled by gas transport to the exterior surface of the sample; a and b – transition zones

The reactions occurring in the gas–graphite system are:

Reactions with oxygen



Where ΔH is the standard enthalpy of formation at 25°C. The above reactions are exothermic and favoured thermodynamically. But carbon does not readily react with air, so kinetic factors are obviously of importance.

Reaction with carbon dioxide

Boudouard reaction:



The equilibrium can be shifted with increasing CO pressure [5, 6] or in the presence of catalyst.

Reaction with water



The hydrogen and CO₂ produced can then react with carbon



The presence of hydrogen can shift reaction Eq. (5) left [6].

Reaction with hydrogen



The mechanism and kinetics of these reactions are described by Walker[7].

The approximate relative rates of gas-carbon reactions at 800°C and 0.1 atm are given in Table 1.

Table 1. Approximate relative rates of gas-carbon reactions at 800°C and 0.1 atm pressure

Reaction	Relative rate
C-O ₂	1x10 ⁵
C-H ₂ O	3
C-CO ₂	1
C-H ₂	3x10 ⁻³

There are a number of investigations of nuclear graphite reactivity under different oxidation conditions in the literature. Results of the oxidation of HTR-10 nuclear graphite IG-11 [8] exhibited three regimes: 400–600°C with activation energy of 158.56 kJ/mol, 600–800°C where the activation energy was 72.05 kJ/mol and a “third-zone” regime above 800°C with very low oxidation energy. A comparison of the reactivity of the two types of graphite used in HTR in oxygen and air at 650–900°C (regime II) leads to the conclusion that there is no difference in the behaviour of matrix graphite (A3-27) and standard graphite V483T during oxidation [9]. In the same time at lower temperature (400°C, regime I), matrix graphite is more reactive with respect to air. For the temperature range of 350–520°C, the activation energy E_a for A3-3 graphite matrix amounts to 110 kJ/mol [10].

B.1.2.2. Liquid-phase reactions

Graphite does not react with alkaline solutions. Oxidising acids attack graphite to different degree, depending on the nature and surface area of the material. The reaction with concentrated nitric acid is:



Depending on the reaction conditions, other products may be formed such as graphitic oxide (C₇H₂O₄), mellitic acid (C₆(CO₂H)₆) and hydrocyanic acid (HCN). Severe oxidation of black carbon by concentrated nitric acid at 100°C gives a group of a few nanometer-sized water-

soluble aromatic compounds [11]. Besides HNO₃, hydrogen peroxide is used for modification of the carbon surface in order to increase the number of functional groups[12].

The simplified reaction with boiling sulphuric acid is the following:



Graphite reacts with ozone dissolved in alkaline solutions with the formation of CO₂ and polycarboxylic acids as degradation products [13, 14].

At 50 to 90°C in alkaline and acid solutions graphite is oxidised with hypochlorous acid HClO forming CO₂ and Cl⁻ [15].

Oxidation of coal by aqueous NaOCl yields several products: black base-soluble, water soluble acids, light-coloured water-soluble acids and CO₂ [16, 17].

B.1.3. Graphite in reactor core structure

B.1.3.1. Design of AVR core structure

The reactor core of AVR represents a cylindrical vessel made of high-purity graphite of 50cm wall thickness which serves as a reflector [18] (Figure 3). The graphite brick reflector vessel is enclosed in a 50 cm envelope made from carbon bricks (graphite with higher amounts of impurities), which provides shielding and heat insulation. All this composition is surrounded by a double-walled steel liner. The bottom and top reflector also consist of graphite and carbon bricks.

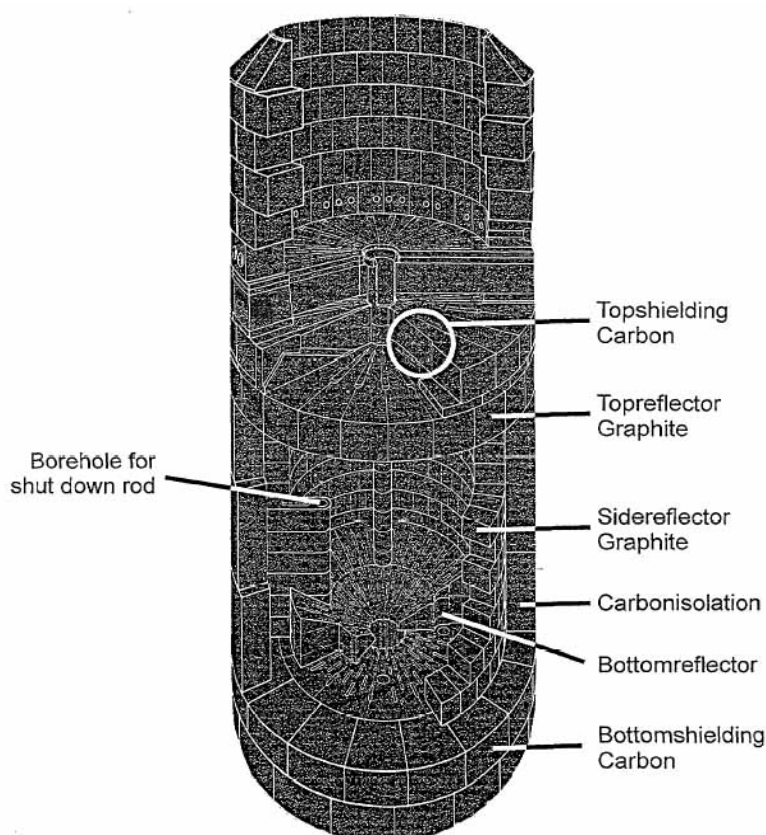


Figure 3. AVR graphite and carbon installations

The reflector of the AVR is made of the graphite quality ARS/AMT produced by Sigris[19]. This graphite is based on needle coke and is densified by extruding, which leads to high anisotropy.

B.1.3.2. Nuclear graphite manufacture

The major processing steps in the manufacture of reflector graphite are summarised in Figure 4. The detailed procedure is described in [20].

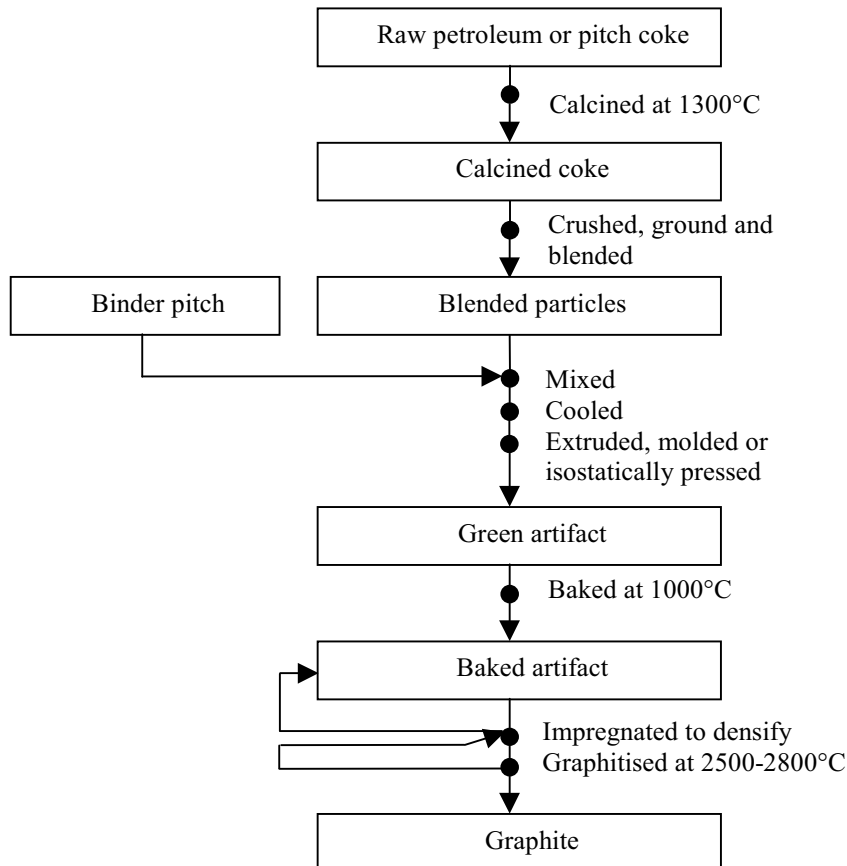


Figure 4. The major processing steps in the production of a conventional polygranular carbon

Polygranular graphite consists of two phases: a filler material and a binder pitch. European nuclear graphites are typically made from a coal-tar pitch-derived coke. The coke is usually calcined at 1300°C before it is crushed and blended. The binder phase is coal-tar pitch. The binder plasticises the filler coke particles so that they can be formed. Commonly used forming processes include extrusion, moulding, and isostatic pressing. The binder phase is carbonised during the subsequent baking operation (~1000°C). Frequently, engineering graphites are pitch-impregnated to densify the carbon artifact, followed by rebaking. The final stage of the manufacturing process is graphitisation (2500–3000°C) during which carbon atoms in the baked material migrate to form the thermodynamically more stable graphite lattice. Nuclear graphites require high chemical purity to minimise neutron adsorption and activation of impurities. Also certain elements catalyse the oxidation of graphite and must be reduced to an acceptable level. This is achieved by selecting very pure cokes, utilising a high graphitisation temperature (>2800°C), or by including a halogen purification stage in the manufacture of the cokes or graphite. All low-boiling point impurities will be removed by graphitisation.

Impurities that remain are those which form carbides or are soluble in graphite. For example, vanadium carbide has a melting point of more than 2800°C; boron carbide melts at 2350°C but also forms a substitutional impurity in the graphite lattice, which is extremely stable.

B.1.4. Graphite fuel elements

The graphitic matrix represents the structural material for the spherical fuel elements of high-temperature reactors (Figure 5). In the inner fuel zone of the elements the matrix serves as a homogeneous envelopment for coated fuel particles. This fuel zone has a diameter of 50 mm and is enclosed in a 5-mm thick fuel-free shell[21].

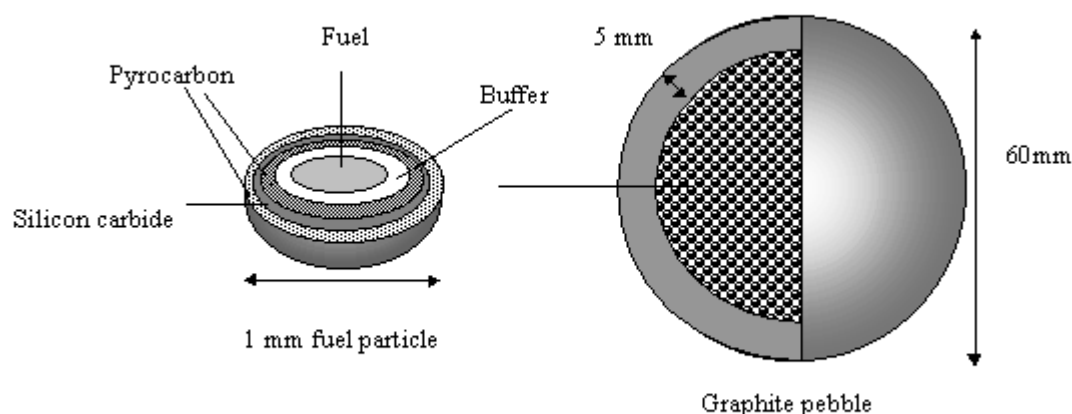


Figure 5. Sectional view of a HTR fuel element

The fuel particles (diameter 200–600 μm) are surrounded by a high-porosity buffer layer to limit the internal pressure from gas production. After the buffer layer they are coated with a high-density pyrocarbon layer (BISO) or with a combination of two pyrocarbon layers with a silicon carbide layer in between (TRISO) to retain radionuclides. In the case of BISO particles, the porous carbon buffer layer is $\sim 80\mu\text{m}$ thick and the pyrolytic carbon layer $\sim 110\mu\text{m}$ thick [22]. In TRISO particles the thickness of the outer and inner pyrocarbon coating layers is ~ 35 and $40\mu\text{m}$, respectively, silicon carbide $\sim 35\mu\text{m}$ and buffer $\sim 90\mu\text{m}$ [23].

B.1.5. Pyrolytic carbon coatings for fuel particles

The development of fuel particles, kernels and coatings processing is described in [24]. Pyrolytic carbon is prepared by the decomposition of a carbonaceous gas over a heated surface. The reaction has been carried out over a wide range of temperatures from 1200 to more than 2000°C. Structure and density of the deposited carbon depend upon the deposition mechanism and deposition conditions. The structure of pyrocarbon deposited in a fluidised bed depends mainly on the pyrolysis gas used, i.e. methane, propane, etc., its concentration, the gas pressure, the carrier gas velocity, the surface temperature, substrate geometry and substrate material.

For example, by methane pyrolysis as a function of temperature and methane concentration three regions with different PyC structure can be distinguished (Figure 6).

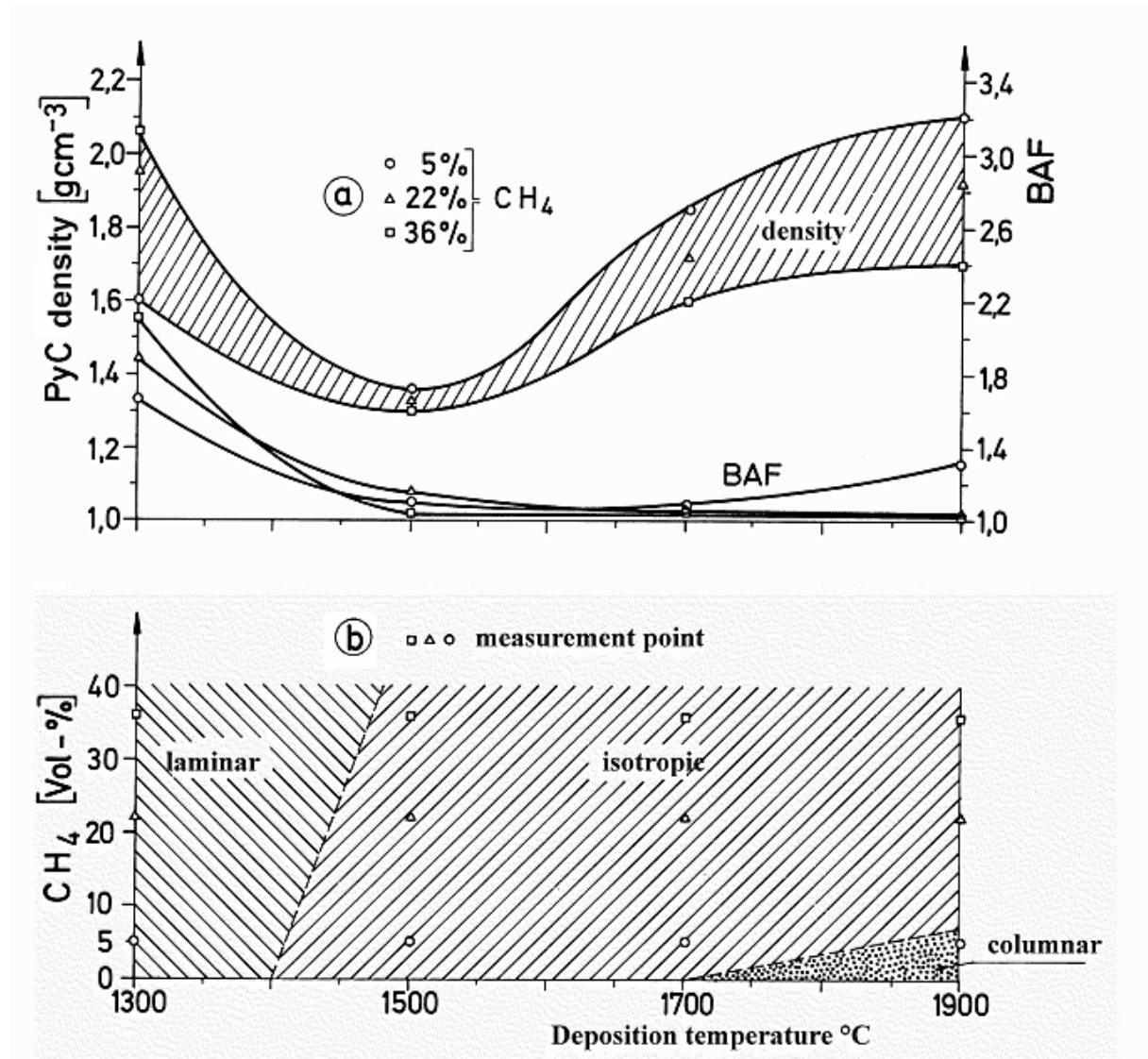


Figure 6. Correlation between pyrocarbon structure, density, BAF and deposition conditions of methane [24]

It is known that isotropic pyrocarbon has the best neutron-irradiation resistance. So the BAF on anisotropy factor (BAF) should amount to 1.0–1.05. The pyrocarbon density that showed the best properties due to the nuclear reactor conditions ranges from 1.75 to 1.95 g cm^{-3} .

From methane deposition, as can be seen in Figure 6, isotropic carbon with such properties can be obtained at temperatures of 1800–2000 $^{\circ}\text{C}$ and methane concentration should be in the range 20–25 vol. %. Pyrocarbon precipitation in the range of higher methane concentration can lead to formation of sufficient amounts of soot to cause a reduction of pyrocarbon density.

Operation at this temperature region of pyrocarbon deposition is not favourable because it is difficult to completely prevent uranium and thorium diffusion in the inner pyrocarbon layer during the coating procedure. Therefore, in the German process of coated particle production the outer and inner pyrocarbon layers of TRISO particles are deposited from a mixture of acetylene, propylene and argon at a temperature of 1300 $^{\circ}\text{C}$ [25].

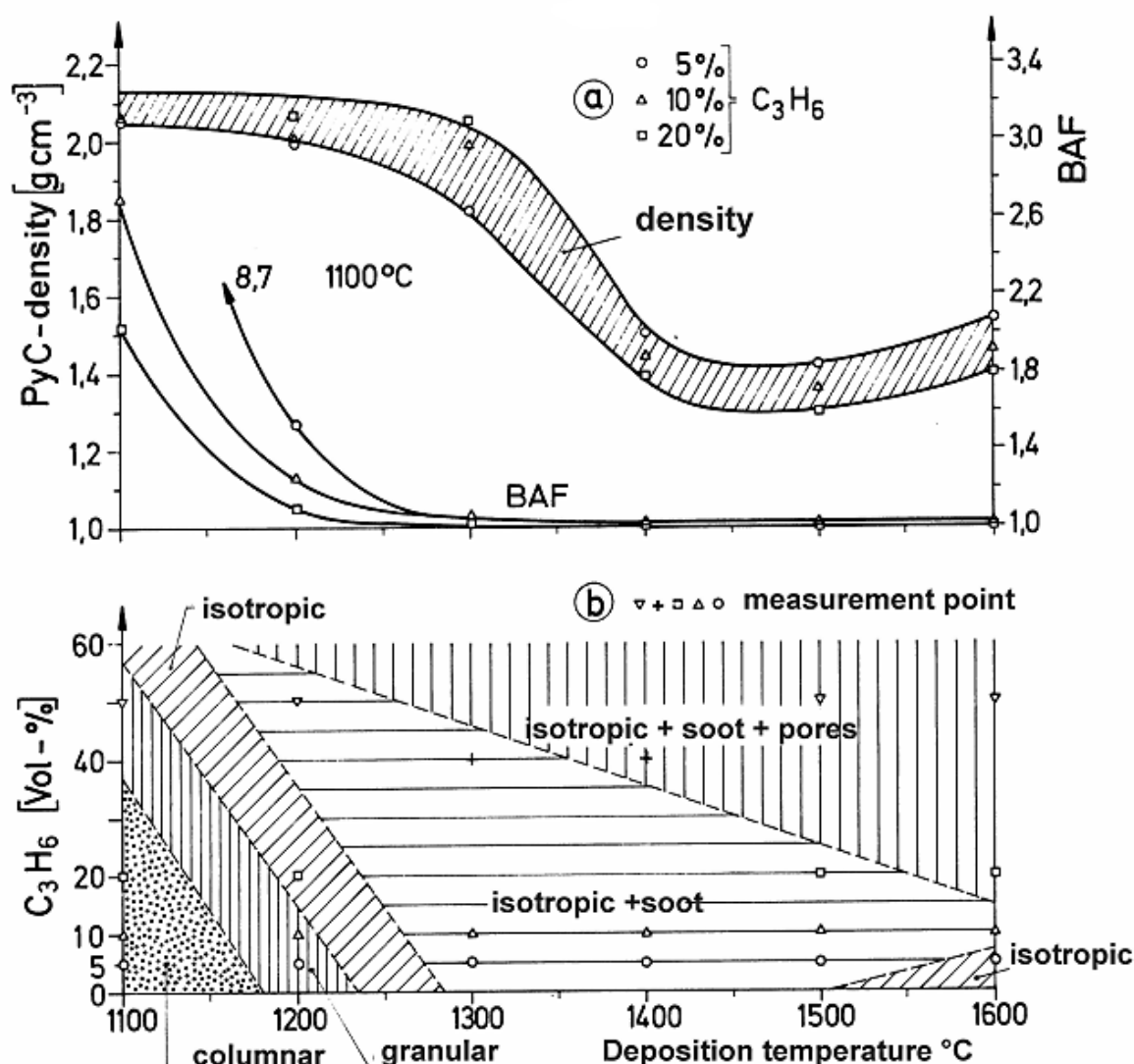


Figure 7. Correlation between pyrocarbon structure, density, BAF and deposition conditions of propylene [24]

Figure 7 shows the dependence of carbon density, structure and BAF on deposition temperature and propylene concentration. In this case, isotropic carbon suitable for application in nuclear reactor is formed in the temperature region of 1200–1350°C. The crystallite size of this pyrolytic carbon amounts to 20 from 60 Å depending on propylene concentrations and fluidised-bed geometry. Pyrolytic graphite has several distinct properties that set it apart from nuclear graphite. They are listed in Table 2.

Table 2. Properties of pyrolytic carbon and nuclear graphite

Properties at room temperature	Nuclear graphite	Isotropic pyrolytic carbon
Density, g/cm ³	1.6-1.81	1.55-2.0
Thermal conductivity, W/m/K	60-105	7.5-12.5
Young's modulus, GN/m ²	8-14	8-9
Thermal expansion coefficient, K ⁻¹	2-5.5·10 ⁻⁶	0.67·10 ⁻⁶
Electrical resistivity, (ohm·cm)	0.7-0.9·10 ⁻³	1.1-1.2·10 ⁻³

B.1.6. Fabrication method of graphite matrix

Several graphitic matrix varieties were developed [21]. In AVR and THTR reactors standard A3-3 and A3-27 matrixes for spherical fuel elements were used. Both materials are based on the same filler components – natural graphite and artificial graphite – and are of similar composition. The essential difference lies in the binder and its processing. For the A3-3 matrix phenolic resin binder is produced from phenol and formaldehyde. The resin is thermoplastic with a two-dimensional cross-linking. The formation of an infusible, hard solid occurs only after heating to 250°C. In contrast, the binder which is synthesised from the raw materials phenol and hexamethylentetramine for the A3-27 matrix is duroplastic with a three-dimensional cross-linking, and hardening of the binder occurs at temperatures >140°C.

The method for fabricating spherical fuel elements was developed and standardized by HOBEG. The process consists of three main steps:

- preparation of the raw material mixture
- moulding of the fuel-free or fuelled spheres
- heat treatment of the spheres

The schema of matrix sphere manufacture is shown in Figure 8. The pre-mixed filler components natural graphite and petroleum coke graphite are kneaded with the dissolved phenolic resin binder, dried and ground in a hammer mill.

For the fabrication of fuel elements, the coated fuel particles are coated with resinated powder prior to processing in a rotating drum, in order to avoid damage due to pressing.

The quasi-isostatic cold-moulding operation, in which dies made of silicon rubber are used, consists of two steps:

1. premoulding of the fuelled zone of the sphere at a low moulding pressure of 0.3 kN/cm²
2. final moulding of the sphere at a moulding pressure of 30 kN/cm² after the fuelled zone has been embedded in resinated powder for the sphere shell

Moulding is followed by mechanical machining of the spheres - lathing to specified size. This is followed by a two-stage heat treatment consisting of carbonisation at 800°C and residual degasification at 1800°C and at 1950°C for A3-3 matrix and only at 1950°C for A3-27 matrix.

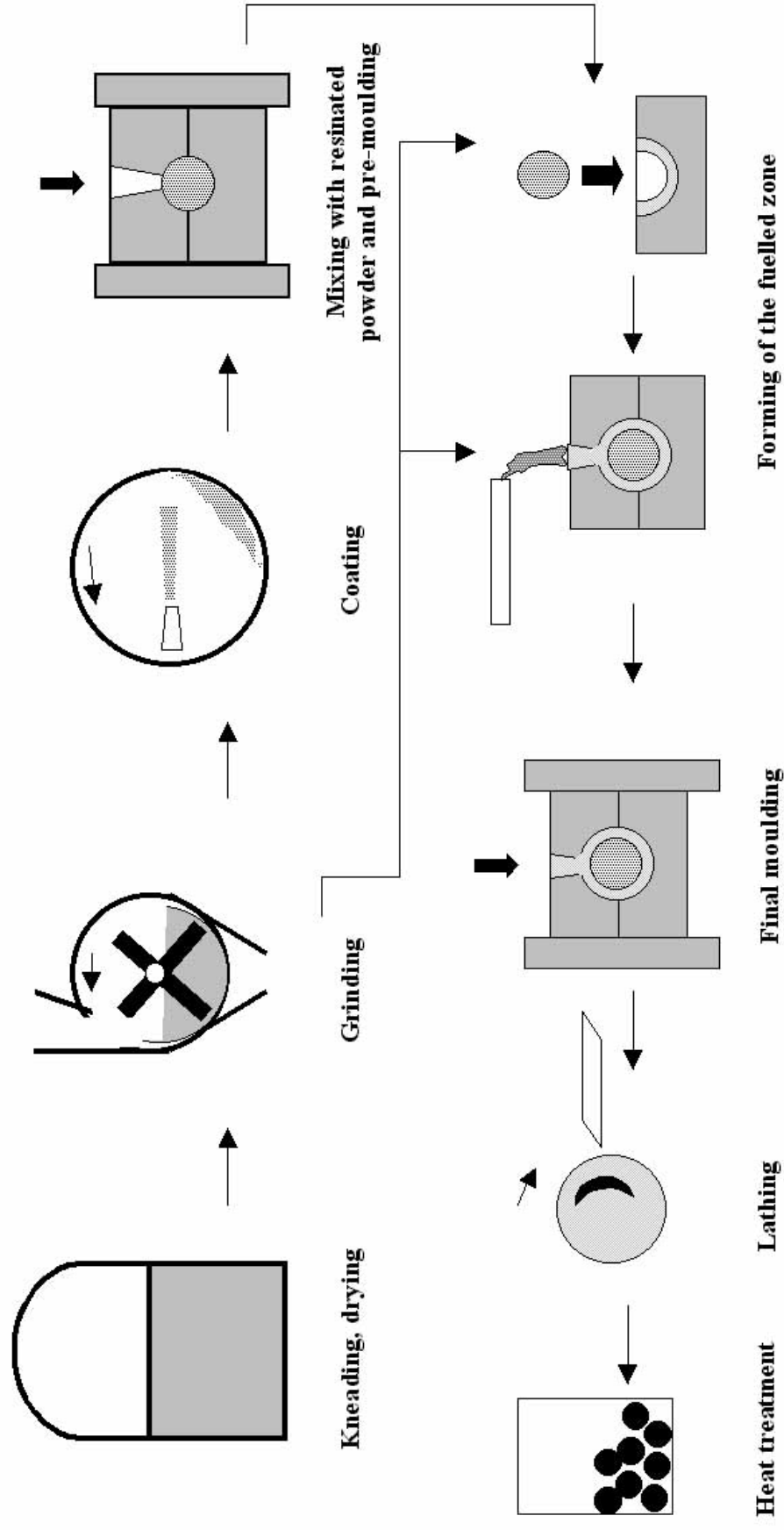


Figure 8. HOBEG method for manufacturing spherical fuel elements

B.2. Graphite waste management

B.2.1. Nature of radionuclide contamination

Radioactivity in graphite and carbon/slag results from the neutron capture reaction on carbon itself and on impurities like cobalt, iron, lithium, nitrogen, etc. In the case of AVR, the impurity concentrations in reflector graphite and insulation layers of carbon bricks are different (Table 3). The other contributions to the total inventory of radionuclides in the graphite must also be considered. Besides the activation of carbon and of stable impurities in the graphite these are the fission of natural uranium present in the graphite as an impurity and the possibility of primarily surface contamination from the other regions of the reactor.

Table 3. Concentrations of impurities in AVR graphite

Concentration, ppm		Activation product
Isolation carbon	Reflector graphite	
30	2	^3H
10	2	^3H
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	$^{93}\text{Mo}, ^{99}\text{Tc}$
1	0.01	^{134}Cs
100	20	^{133}Ba
2	0.02	$^{151}\text{Sm}, ^{155}\text{Eu}$
0.1	0.02	$^{152}\text{Eu}, ^{154}\text{Eu}$

Tritium

The radionuclide ^3H , tritium has a half-life of 12.3 years. The contribution of radioactivity in nuclear graphite arising from tritium is significant [26-28]. It is produced by the following reactions:

- fission reaction, such as $^{235}\text{U}(\text{n},\text{f}) ^3\text{H}$ reactions,
- $^6\text{Li}(\text{n},\alpha) ^3\text{H}$ reactions, lithium is present as an impurity in the graphite matrix of the fuel element and in the reflector,
- $^3\text{He}(\text{n},\text{p}) ^3\text{H}$ reactions of the ^3He isotope present in the helium coolant,
- $^{10}\text{B}(\text{n},2\alpha) ^3\text{H}$ reactions in the absorber rods (negligible for designs without core rods).

Main contribution to accumulation of tritium in graphite is given by neutron reactions with ^6Li and ^3He nuclei. Tritium generated from lithium impurities present in graphite is mostly produced in the graphite bulk. The release of tritium is controlled by its diffusion out of the grain boundaries and into the pore system.

The chemical properties of tritium are essentially the same as those of ordinary hydrogen. One of the most important reactions is isotopic exchange where tritium can replace hydrogen atoms in water molecules or in organic molecules. The exchange process Eq. (10) is rather slow at room temperature (equilibrium constant $K=6$ at 25°C) because the hydrogen is tightly bound.



Radiocarbon

Radionuclide ^{14}C has a half-life of 5730 years. It is mainly produced in the reactor graphite through the following neutron reactions:

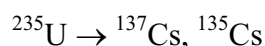
Table 4. Activation reactions producing ^{14}C

Reaction	Capture cross section in barns (10^{-24}cm^2)	Abundance of isotope in %
$^{13}\text{C} (\text{n}, \gamma) ^{14}\text{C}$	$0.9 \cdot 10^{-3}$	1.1 ^{13}C /carbon
$^{14}\text{N} (\text{n}, \text{p}) ^{14}\text{C}$	1.81	99.63 ^{14}N /nitrogen
$^{17}\text{O} (\text{n}, \alpha) ^{14}\text{C}$	0.235	0.04 ^{17}O /oxygen

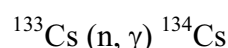
In the reactor core materials nitrogen is present only as an impurity, whereas carbon and oxygen are in some cases major constituent elements of the coolant, moderator or fuel. In spite of this fact, the ^{14}N activation reaction is usually the most important contributor to ^{14}C production because of its larger cross section and high isotopic abundance of ^{14}N in natural nitrogen. Nitrogen in graphite is in the bound state, substituting for carbon atoms in the nodes of crystal lattice, or in a gaseous form filling pores in graphite. The kinetic energy of the ^{14}C atom formed is about 470 kJ/mol. This value is equivalent to the bond energy between C–C bond and C=C bond. It was suggested [29] that the ^{14}C atom formed stays in the same position as ^{14}N . Thus the level and location of nitrogen impurity in all reactor core materials is an important parameter. The nitrogen levels vary widely from 10 to 100 ppm in different reactor graphites [30] and sometimes they are not known very precisely. It was shown that the nitrogen content is the largest on the surface [29]. From the surface to a depth of about 30 nm, the nitrogen concentration decreases.

Caesium

The three radioactive caesium isotopes ^{134}Cs , ^{135}Cs and ^{137}Cs are produced by nuclear fission and neutron capture reactions:



^{134}Cs can be also produced from the stable isotope impurity during reaction:



The half-life of Cs isotopes is two years for ^{134}Cs , $2 \cdot 10^6$ for ^{135}Cs and 30.1 for ^{137}Cs . The sources of radioactive Cs contamination are: uranium impurities in reactor graphite, uranium

present in the circuit from fuel elements externally contaminated during manufacture, volatilisation of Cs from defect fuel due to its high vapour pressure. This Cs can be absorbed in graphite and form the interstitial compounds [31].

Europium

^{152}Eu , ^{154}Eu , ^{155}Eu are produced by fission reaction and their half-lives amount to 12.4 years, 8.5 years and 4.5 years respectively. The isotopes can be also formed by activation of the impurities ^{151}Eu , ^{153}Eu and ^{154}Sm .

Cobalt

^{60}Co originates from neutron activation of stable ^{59}Co , which is present as an impurity in nuclear reactor graphite, and has a half-life of 5.3 years.

Table 5 shows the calculated total radioactivity in AVR graphite at the end of 1988 [32].

Table 5. Total radioactivity in AVR graphite

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

B.2.2. Diffusion of radionuclides in graphite

Diffusion can be defined as the mechanism by which matter is transported into or through matter.

In polycrystalline materials the mechanism of diffusion is very complex. Different types of diffusion are distinguished upon the kind of the medium, and differ in the progressive motion of the atoms and in the rate of diffusion. *Volume diffusion* describes progressive movement of atoms in a solid with regular lattice structure. The movement of atoms in crystals is possible

mainly due to the presence of different kinds of defects. Different motion possibilities exist for the lattice's own atoms as well as for foreign atoms [33] (Figure 9):

- a) when an atom is displaced from the lattice site and jumps to neighbouring vacancies or interstitial position.
- b) when there is an exchange of lattice positions involving two, three or four atoms situated next to one another in the crystal structure.

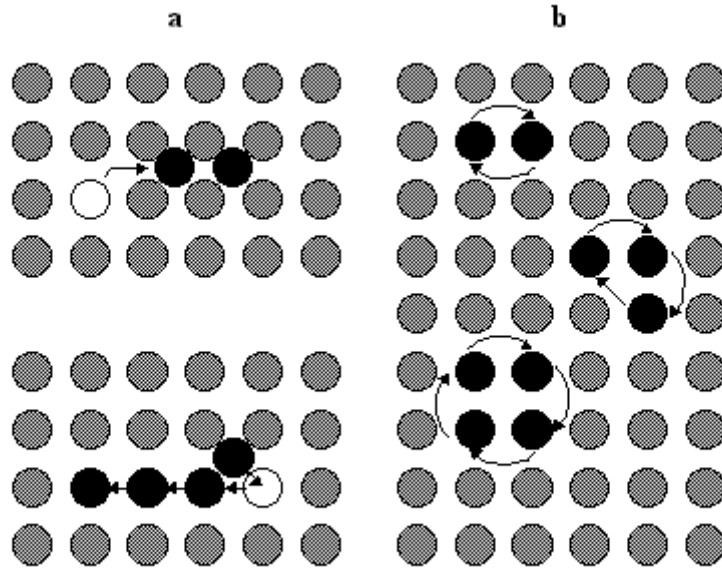


Figure 9. Atom movement in crystal lattice: a) jump to neighbouring vacancies or interstitial position, b) exchange of atoms

The other type of diffusion connected with structure of solid substance is *grain boundary diffusion*. An illustration of the porous structure of graphite is shown in Figure 10. It consists of granules of around a few microns in size with voids in between. The granules themselves are made up of small crystallites. The volume diffusion takes place inside these granules. The demarcation of grains from each other leads to free space, which together with grain surfaces is included in the term the “grain boundaries”. The rate of *diffusion along grain boundaries* is much faster than that of diffusion in the bulk crystal.

Pore diffusion plays a role in porous materials. If the diffusing atoms form a bond with the grain surface, the mechanism of grain boundary diffusion will be valid. In the case of noble gases (Kr, Xe), when there is no chemical interaction with the surface of material, an unhindered transition of fission gases occurs from grains to pores. Then a free movement of the diffusing atoms is possible as in a gas. Therefore pore diffusion can be compared with the diffusion in gas phase.

The behaviour of radionuclides in graphite at high temperatures is of great importance. It depends on the properties of the diffusing substance. The temperature dependence of the diffusion coefficient is expressed by the Arrhenius equation:

$$D = D_0 e^{-\frac{E_a}{RT}} \quad \text{Eq. (11)}$$

where D_0 – pre-exponential factor, E_a diffusion process activation energy.

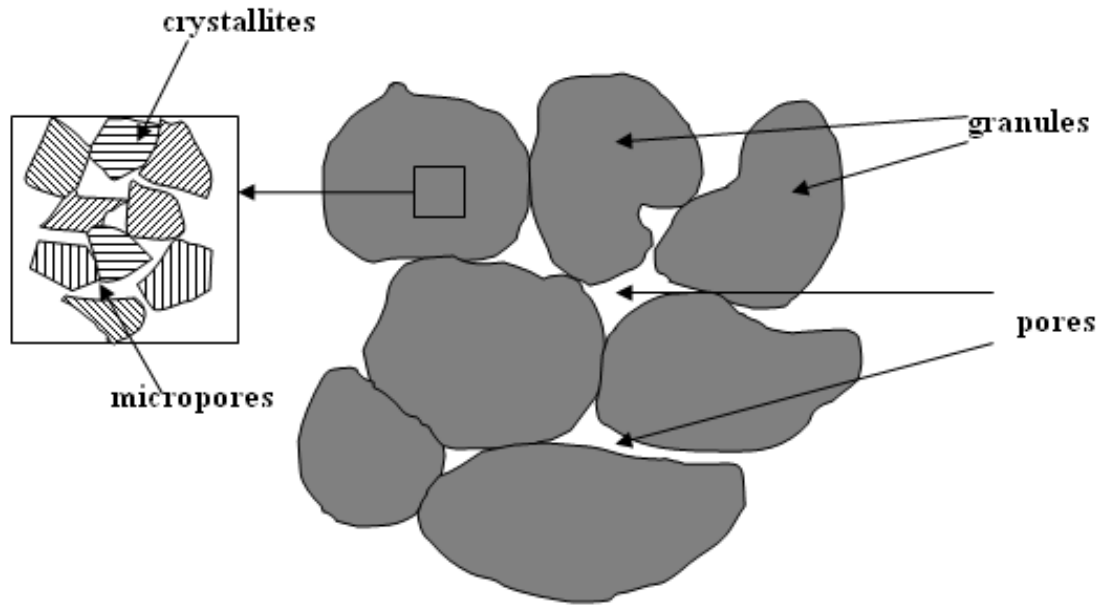


Figure 10. The porous structure of graphite

Reduced diffusion coefficient D' (s^{-1}) is defined as the diffusion coefficient D (m^2/s) divided by the squared “equivalent sphere” diffusion radius, a (m):

$$D' = \frac{D}{a^2} \quad \text{Eq. (12)}$$

The self-diffusion in graphite becomes essential above 2150°C. The diffusion coefficient at 2200°C was determined to be in the range $6.4 \cdot 10^{-16}$ to $3 \cdot 10^{-15}$ cm^2/s for different types of nuclear graphite [34].

Studies of the release behaviour of different radionuclides from graphite have been made. Diffusion coefficient for strontium in LTI pyrocarbon (low temperature isotropic) varies from 10^{-12} to 10^{-8} cm^2/s in the temperature range 300–730°C. In graphite strontium diffusion is faster – diffusion coefficient amounts to 10^{-11} – 10^{-6} cm^2/s for the same temperature [35].

Caesium release from BISO coated particles is 32% after 1 hour of post-irradiation annealing at 2300°C, and europium release 23% after 3 hours [36]. In the pyrocarbon layer, the caesium diffusion coefficient was $4 \cdot 10^{-11}$ – $3 \cdot 10^{-8}$ cm^2/s at temperatures of 1600–2200°C.

The experiments with irradiated BISO particles (FIMA 14%) showed that Sr and Cs were released almost quantitatively at 2000°C after 5 hours. 72% of the caesium was released and 26 % was retained in the pyrocarbon layer. The release of Sr was about 92% [37].

Caesium is a very mobile element. During the procedure of graphite burning Cs can be released from the graphite matrix, volatilised (Cs vapour pressure is 0.1 atm at 750°C) and transported from the furnace into the off-gas [26, 38]. The loss of Cs from graphite due to vaporisation was 15 % of the total amount at 750°C after 9 hours of annealing [39]. The vaporisation of Sr and Ba from the graphite body starts above 1200°C [39]. From 200 °C to 1200°C, atoms of Ba move inside the graphite to active sites and can be leached out later.

Tritium emission from Windscale Pile I graphite was studied by Wörner et.al. [40]. After 30 min at 700 °C about 3% of the tritium was released.

Tritium behaviour in reactor graphite is discussed by Fischer and Malka [41, 42]. The reduced diffusion coefficient of tritium from pitch coke AS1-500, petroleum coke AL2-500 and graphite matrix A3-3 was determined (Table 6). The experiments were performed after irradiation of graphite in FRJ-1 (AS1-500 and A3-3) and AVR (AL2-500). In the first case, the temperature during irradiation did not exceed 100°C (cold irradiation). In the case of AVR the irradiation temperature was about 500°C.

The diffusion process of tritium depends strongly on the nature of the graphite samples [43, 44]. As was shown [44] the release behaviour depends strongly on the extent of graphite anisotropy and the diffusion of tritium in isotropic graphite will be faster than in anisotropic graphite.

Table 6. Diffusion coefficients of nuclear graphite

Type of graphite	Temperature, °C	Diffusion coefficient, D' s ⁻¹
A3 ¹⁾	800	1.72E-09
A3 ¹⁾	850	9.09E-09
A3 ¹⁾	900	6.89E-08
A3 ²⁾	1000	8.18E-09
AS1-500 ²⁾	1050	9.83E-11
AL2-500 ²⁾	1025	1.83E-10

1) - [42], 2) - [41]

B.2.3. Options of graphite waste management

The management options considered for graphite waste [28, 45] are as follows:

- disposal on the deep ocean bed
- shallow land burial
- incineration
- deep geological disposal (inland site and coastal site)

Ocean-bed disposal

Disposal of graphite on the deep ocean bed would lead to a slow release of activity into bottom waters by leaching, and gradual dispersal throughout the world's oceans. The main contribution to collective doses would be the global circulation of ¹⁴C.

Shallow land burial

The shallow land burial facility is assumed to be a fully engineered concrete structure incorporating barriers against infiltration of groundwater, and located in a clay formation with relatively low groundwater flow. The possibility of long-term leaching of activity from the graphite by groundwater, followed by movement to the soil zone and into crops and drinking water must be considered. Also the long-term environmental risk remains (thousands of years) because material is not truly isolated from the environment.

Incineration

This option for graphite processing enables the volume of radioactive wastes to be reduced. However, CO₂ formed leads to the release of ¹⁴C into the atmosphere. ¹⁴CO₂ penetrates into the metabolism of the plant and animal world by photosynthesis. Because of its long half-life and the biological significance of carbon, the release of ¹⁴C from nuclear facilities could have a major radiological impact on the environment and mankind.

Deep geological disposal

Two different types of deep geological disposal were considered. The first is an inland site in different rock units, which could lead to very long transit times for radioactivity transported by moving groundwater. The second – a coastal repository – is assumed to be sited in shale. Here water movement can be relatively fast and the risk of radionuclides transport to biosphere will be also higher.

In the frame of the present work the graphite incineration and storage in deep geological formation will be viewed in more detail in Chapter B.2.4 and Chapter B.2.5.

B.2.4. Reprocessing of contaminated graphite

In the context of the final disposal route it is important to reduce waste volume. Processing of graphite by incineration offers the opportunity to separate the major fraction of the graphite mass from the short-lived radioisotopes [46]. Only small residues (ash) remain for final storage. However, the release of ¹⁴C into the atmosphere accompanied by graphite burning is unfavourable.

J.B. Mason and D. Bradbury [47] suggested burning waste graphite without CO₂ release into environment. This methodology involves the use of pyrolysis/water steam reforming followed by off-gas control. The exhaust gas can be solidified in the form of calcium carbonate, which could be used to fill voids in other radioactive waste packages. It was suggested that the process could either be used to process graphite removed from the core or even applied to gasify graphite waste within the core.

Two options have been considered for the conversion of carbon dioxide to an alkaline earth carbonate [48]. The first is direct precipitation:



(M = Ca, Sr or Ba).

The second alternative is the double alkali process. In the first step, carbon dioxide is adsorbed by sodium hydroxide solution. The resulting sodium carbonate then reacts with an alkaline earth hydroxide in a separate vessel to precipitate the carbonate and regenerate sodium hydroxide for recycling:



However, reprecipitation of carbon dioxide in carbonate form does not solve the problem of volume waste reduction. Moreover, carbonate wastes are less stable to leaching than graphite in elementary form. The dissolution rate of CaCO₃ reported in [49] amounts to 5.94·10⁻⁷ mol/(cm²·d). For MgCO₃ it was found to be ~10⁻⁷ mol/(cm²·d) in the pH range 0–4

and $\sim 10^{-9}$ mol/(cm²·d) in the pH range 5–8 [50]. Whereas the graphite oxidation rate in pure water was determined as $\sim 10^{-11}$ mol/(cm²·d) [51].

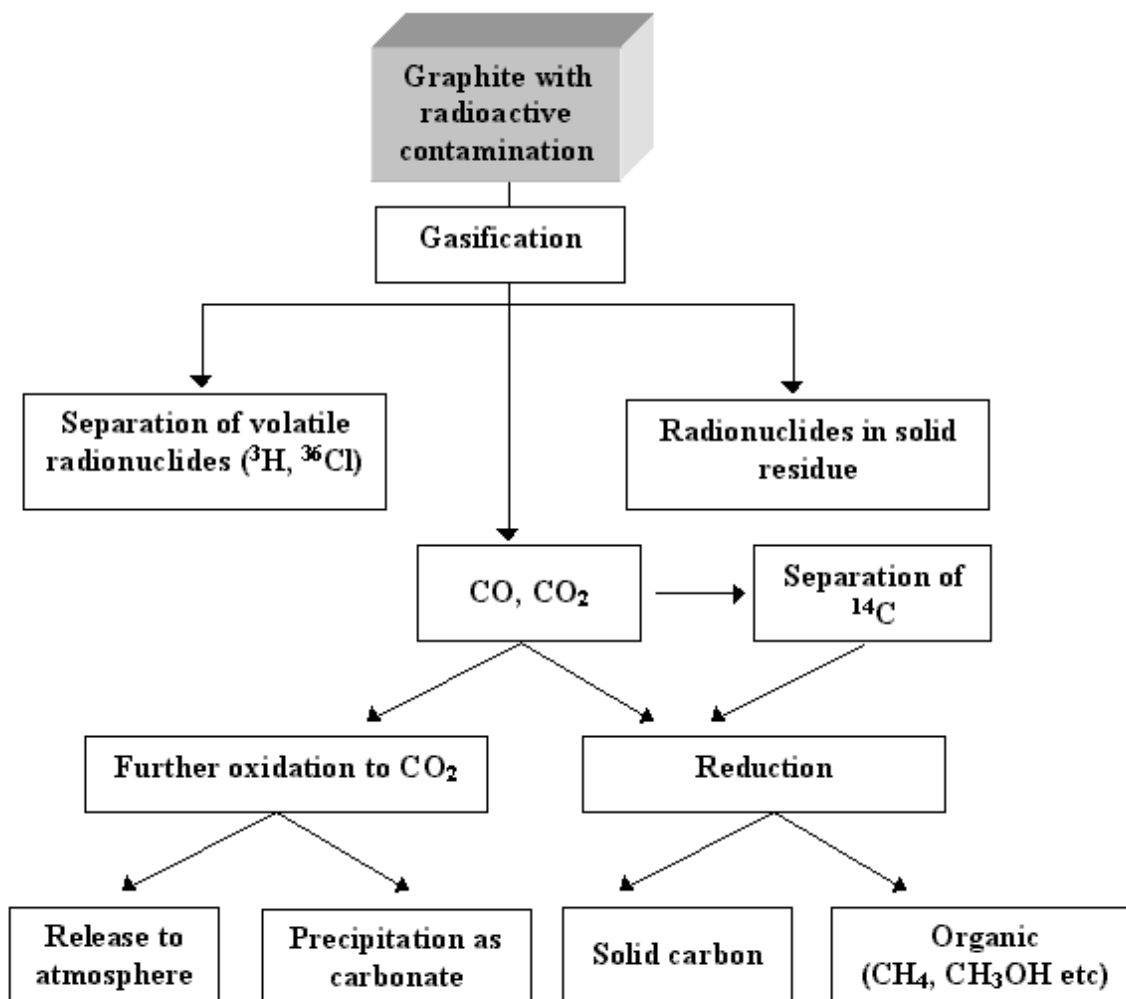


Figure 11. Graphite treatment scheme

Carbon from the gas phase can be precipitated in the form of elementary carbon as likely to be resistant to leaching. Contaminated graphite reacts with water steam in a fluidised bed with the formation of CO. Elementary carbon can be obtained from carbon monoxide by the Boudourd reaction:



This reaction is exothermic from left to right. High conversion of carbon monoxide to carbon is possible at a relatively low temperature in the presence of a catalyst [52, 53]. The problem is that only half of the carbon reacting will be immobilised as a solid. The other half (as carbon dioxide) would have to be recycled. The preferred procedure in this case is gasification of graphite with H₂ in order to form methane. Subsequent pyrolysis of methane yields elementary carbon in the form of soot.

The general scheme of graphite reprocessing with subsequent separation of radionuclides is presented in Figure 11.

B.2.5. Deep geological disposal

B.2.5.1. Host rock types

For the purpose of waste disposal in geological formation three types of rocks (argillaceous or “clay-rich” units, hard crystalline igneous and metamorphic rocks, and evaporites – halite formation) are considered as host units. All of them have a low permeability and therefore low rates of water through-flow in terms of volume and velocity.

Hard stable crystalline rocks (granite, gabbro and basalt) have low total porosity. However they are generally joined and fractured. Water flow through the rock is dominated and controlled by these fissures. Therefore crystalline rocks can be considered more or less permeable, although the contribution of the fracture to the porosity of these rocks is small.

Argillaceous rocks, although they differ in physical properties, ranging from plastic clays to hard, well-bedded and often fractured units, are characterised by low permeability and high sorption capacity (radionuclide retardation potential).

Evaporite (salt) deposits were thought to be completely impermeable and they also have the additional advantage of being plastic enough to allow self-sealing of fractures by creep in response to heat and stress. Evaporites are units of soluble salts of Na, Mg, K and Ca formed in the geological past by evaporation of shallow lagoons and lakes in cyclic episodes. Chlorides, sulphates and carbonates may be laid down in layers with various degrees of mixing of salts. The most common salt is halite rock salt, NaCl. So the composition of corrosive groundwaters will be determined by the chemistry of salt with which they interact.

For heat-generating radioactive waste forms, salt rock, for example such as Gorleben salt dome [54, 55], is considered to be a good host medium because of the unique viscoplastic properties which, with lithostatic pressure plus temperature as the driving forces, will build up a natural barrier within a few years after emplacement of the waste packaging.

B.2.5.2. Multi-barrier system

Conservative assumptions on scenarios for post-operational period are made for the long-term safety considerations. It is presumed that water can penetrate into the repository due to consequences of engineering and waste replacement. Water intrusion may produce a harmful effect on the integrity of the waste forms and in the course of time lead to mobilisation of radionuclides.

The repository design should ensure long-term isolation of the waste and thus comprise a system of geological and engineered barriers to prevent the release of the waste from the packages and the movement of radionuclides to biosphere. The multi-barrier system includes four components (Figure 12).

The first is the waste form itself, which immobilises the waste radionuclides in a solid matrix. In the case of HTR fuel element it has its own subsystem of protective layers: graphite matrix, dense pyrocarbon coating, silicon carbide layer, porous pyrocarbon coating (buffer), and fuel in the form of the stable leach resistant ceramic.

The second barrier is the metallic canister in which the waste will be sealed. To minimise water movement around the container and to ensure that the waste block is in mechanical and thermal continuity with the rock, it is necessary to fill the emplacement hole with some backfill material – third barrier. The back-fill material should also possess a good adsorptive activity towards the radionuclides, which may be leached from the waste package. The waste matrix, container and back-fill material are termed the “engineered barriers”.

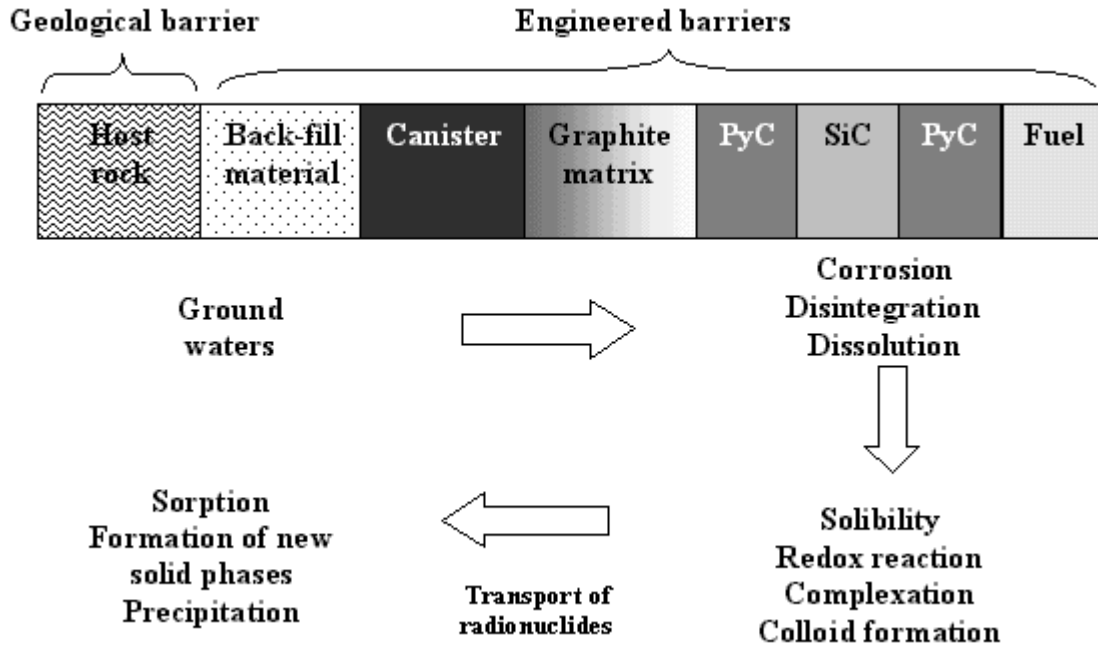


Figure 12. Migration and immobilisation of radionuclides in the multibarrier system

The final barrier is the host rock and geological environment (geological barrier) in which the repository is constructed.

B.2.5.3. Water radiolysis in repository

In a final repository an aqueous phase, which may migrate towards the radioactive waste package, will be irradiated by spent fuel elements. The radiolysis of water produces both molecular and radical oxidants and reductants [56], which may influence the redox conditions in the repository and the stability of the waste form, container and buffer materials.

Radiolysis of pure water

The radiation chemistry of water and aqueous solutions is usually described in terms of the spur diffusion model.

Several pairs of radicals or ions (primarily e^-_{aq} , $OH^\bullet$ and H_3O^+ in pure water) are formed in small isolated volume elements (spurs) in the initial radiation process. Species within the spurs interact as they diffuse into homogeneous distribution and these interactions result in the reformation of water and in the formation of molecular products. In pure water under γ -irradiation the decomposition products which appear in homogeneous distribution are e^-_{aq} , $OH^\bullet$, H_2 and H_2O_2 .

The overall process of radiolysis is usually divided into three stages.

The *physical* stage consists of energy transfer to the system. Its duration is of the order of 10^{-15} sec or less. Ionisation or excitation of water takes place



The *physicochemical* stage consists of processes, which lead to the establishment of thermal equilibrium in the system. Its duration is of the order of 10^{-11} sec or less. Electrons ejected in the ionisation process become thermolised and hydrated:



The H_2O^+ ions undergo a proton transfer reaction with neighbouring water molecules:



and the H_3O^+ becomes hydrated.

The dissociation of excited water molecules gives the hydrogen atom and hydroxyl radical as main products



It also gives a low yield of hydrated electrons and, eventually, molecular hydrogen. The contribution of excited water molecules to the formation of primary free-radical products in water radiolysis is of minor importance in comparison with that of the ionisation processes.

The *chemical* stage consists of diffusion away from the point of origin and chemical reaction of primary species (e^-_{aq} , $\text{OH}\cdot$, H_3O^+ and H), and leads to the establishment of chemical equilibrium. It begins in the spur about 10^{-11} sec after the passage of the radiation and about 10^{-10} sec in the bulk of the solution. The radiation-chemical yield of primary species G is determined as the number of species produced or disappearing per 100 eV of energy absorbed.

Molecular hydrogen is formed from recombination:



The first reaction is the most important.

Atomic hydrogen arises primarily from Eq. (20) and reaction Eq. (24):



The recombination of hydroxyl radicals is the way to give hydrogen peroxide as the final product.



Important water reformation reactions are



The principal radiolytic products in pure water or dilute aqueous solutions are listed in Table 7.

Table 7. Primary products in irradiated water

Irradiation	G-Values (molecules per 100 eV)						
	H ₂	H•	e ⁻ _{aq}	H ₂ O ₂	OH•	HO ₂ •	H ⁺
γ	0.43	0.61	2.7	0.61	2.86	0.03	2.7
α	1.4	0.3	0.3	1.3	0.5	0.1	0.3

Radiolysis of salt brines

Reactive solutes at high concentrations can react with radicals and thus change G-values from those in pure water and cause the formation of additional G-species.

In concentrated neutral chloride solution OH radicals will be removed by the reaction Eq. (29) [57]:



In acid solution this reaction will be also of significance. It will cause a reduction of OH• and H₂O₂ production from that in pure water and will promote the increase of e⁻_{aq} and H₂. High hydrogen production has been observed in the γ- and α-radiolysis of brines [45]. Also chlorate, hypochlorite and chlorite can be formed as stable products [58]. Formation of hypochlorite can be related to the chain of reactions, which take place during γ-irradiation of chloride solutions:



Chlorate can be formed from Cl₂ through reactions involving radicals; it can be formed from Cl₂ by hydrolysis:



The radiation chemical reactions occurring in the presence of Cl⁻ ions were published by Sunder [59]. The formation of different chlorine oxidising species is associated with a high redox potential which can reach 1200 mV [45, 60]. Under such conditions the behaviour of protective barriers can differ from those in the absence of γ-irradiation.

C. Experimental part

C.1. Equipment

The following technical equipment was used:

Drying oven	Heraeus T-12
Gas chromatograph	1: SiChromat 2 from Siemens separating columns: Porapak QS (80/100 mesh, L=1 m, ID=2mm) and molecular sieve 5 Å (80/100 mesh, L=2x3 m, ID=2 mm) carrier gas: argon 2: SiChromat 2 from Siemens separating columns: Poraplot Q (L=10m, ID=0.32mm) and molecular sieve 5 Å (25 m, ID=0.32mm) carrier gas: helium
Optical microscope	Karl Zeiss KS300 with image processing software (KS300)
Scanning electron microscope (SEM)	Jeol JSM 840 coupled with EDX unit Tracor Northerm 5502
Furnace	combustion furnace C-5500 from Ströhlein Instruments; tube furnace, adjustable up to 1550°C
BET surface area measurements	Junior Quantosorb, QUANTOCHROM
Balance	MP-3000, YMC Europe GmbH
Liquid scintillation counting (LSC)	TRICARB 2100, Packard
CO, CO ₂ analyser	NGA 2000 MLT analyser from Fisher-Rosemount, concentration range 0–4000 ppm
Flow controller	mass flow controller 5850E, Brooks fluid: air range: 0–80 L/h
γ-spectrometer	High-Purity Germanium Well Detector from EG&G Ortec
X-ray diffraction (XRD)	Stoe Stadi transmission diffractometer coupled to a Cu-anode X-ray tube and using CuKα radiation with $\lambda = 1.5406 \text{ Å}$ at 40 kV and 30 mA
Water purification	Elga Elgastat maxima HPLC specific resistance of purified water is 18.2 mΩ

C.2. Reagents and materials investigated

The following chemicals were used:

MgCl ₂ ·6H ₂ O	K ₂ SO ₄	HCl
CaCl ₂ ·2H ₂ O	NaOH	HNO ₃
NaCl	MgSO ₄ ·7H ₂ O	H ₂ O ₂
KCl	CuO	

All chemicals were from MERCK, Darmstadt, and of analytical grade. They were used without preliminary treatment.

Investigated materials:

Graphite matrix A3-3:	graphite powder
Pyrocarbon:	coatings from unirradiated BISO fuel particles, intact BISO and TRISO particles (dimensional characteristics are listed in Table 33, appendix)
Merlin reactor graphite:	bottom right channel of thermal column II
AVR graphite:	inner reflector

Gases:

Argon:	purity >99.999%, MESSER Grisheim
Oxygen:	purity >99.5%, LINDE
Calibration gas:	mixture CO – 1880 vpm, CO ₂ – 2180 vpm, O ₂ – 0.516 vol%, H ₂ – 4 vol%, N ₂ – rest; MESSER Grisheim

Preparations of brines

Brine-2. 937.08 g MgCl₂·6H₂O was mixed with 300 mL of deionised water heated up to 70°C and stirred until the main part of the magnesium chloride was dissolved. Then 0.126 g MgSO₄·7H₂O, 4.13 g NaCl, 1.42 g KCl and 39.68 g CaCl₂·2H₂O were added. Stirring was stopped when the solution became clear. After cooling to room temperature, the solution was placed in 1 L volumetric flask and water was added to the filling mark.

Brine-3. 309.4 g NaCl was dissolved in 0.5 L of deionised water and stirred at 70°C up to complete dissolution. Then 2.74 g CaCl₂·2H₂O, 2.83 g K₂SO₄ and 4.0 g MgSO₄·7H₂O were added. When the solution was clear it was cooled down and placed in 1L volumetric flask and the water level was brought up to the filling mark.

The compositions of the aquatic phases are summarised in Table 8.

Table 8. Composition of aqueous phases [61]

	NaCl	KCl	K ₂ SO ₄	MgCl ₂	CaCl ₂	pH(90°C)
	Concentration mol/1000mol H ₂ O					
Brine-2	1.49	0.4	–	97.21	5.68	3.61
Brine-3	108.65	–	0.67	0.32	0.38	7.07

C.3. Performance of experiments

C.3.1. Graphite oxidation

C.3.1.1. Sample preparation

Graphite was filed from a dummy fuel element on a turning lathe. The graphite powder was separated by sieving into different fractions with particle size: >0.8 mm, 0.8–0.5 mm, 0.5–0.25 mm, 0.25–0.15 mm, 0.15–0.05 mm, <0.05 mm.

Pyrocarbon coatings were obtained from disintegration of unirradiated BISO fuel particles. Fuel particles were disintegrated by mechanical cracking in a milling machine. After separation the coatings were additionally milled in mortar.

C.3.1.2. Oxidation experiments without irradiation

Two different series of experiments were performed:

- long-term experiments
- short-term experiments

Long-term experiments were performed in glass tubes at 90°C under different atmospheres. 1 g of graphite or pyrocarbon was immersed in 50 mL of aqueous phase in a glass vessel with a total volume of 110 mL. Then the tubes were evacuated, filled with Ar, O₂ or air and sealed by melting. The experimental details are summarised in Table 26 (see Appendix).

Short-term experiments were performed with the addition of different concentrations of H₂O₂ (10^{–3} mol/L, 10^{–2} mol/L, 2.1·10^{–2} mol/L, 3.2·10^{–2} mol/L, 5.4·10^{–2} mol/L, 1.1·10^{–1} mol/L, 1.6·10^{–1} mol/L, 2.7·10^{–1} mol/L) to simulate the radiolysis process. 1 g of graphite powder fraction <0.05 mm was placed in glass vessels with 20 mL of distilled water and brine-2 solution. Then 30% H₂O₂ was added in amounts from 2 µL to 500 µL and the system was evacuated, flushed with argon a few times, finally filled with argon and closed. The experiments with hydrogen peroxide were performed in glass vessels with valves. The volume of the glass vessels was 36 mL.

C.3.2. Oxidation experiments under γ-irradiation

Experiments with graphite powder, pyrocarbon coatings and also with intact graphite pieces and intact unirradiated fuel TRISO and BISO particles were performed under γ-irradiation in the MTR cooling pool. 1 g of carbon coatings or graphite powder and 10 mL of liquid phase (distilled water, brine-2 or brine-3) was placed in glass vessel with a total volume of 36 mL. The amount of material taken was about 0.1 g in the case of intact particles and graphite pieces. Glass vessels with aqueous phase and carbon material were evacuated, filled with

argon and sealed. Sealed vessels were placed in an inner irradiation container (Figure 13). The container was equipped with a heater in order to maintain the temperature at 90°C. It was placed in an outer irradiation container and then in the MTR cooling pool. The irradiation was produced by four spent MTR fuel elements situated along the perimeter of the container. All experimental equipment and the position of container in the cooling pool are shown in Figure 14. The scheme of the irradiation containers with heating system is also presented in Figure 49 in Appendix.



Figure 13. Glass tubes used for experiments in MTR cooling pool (left) and container with glass tubes (right)

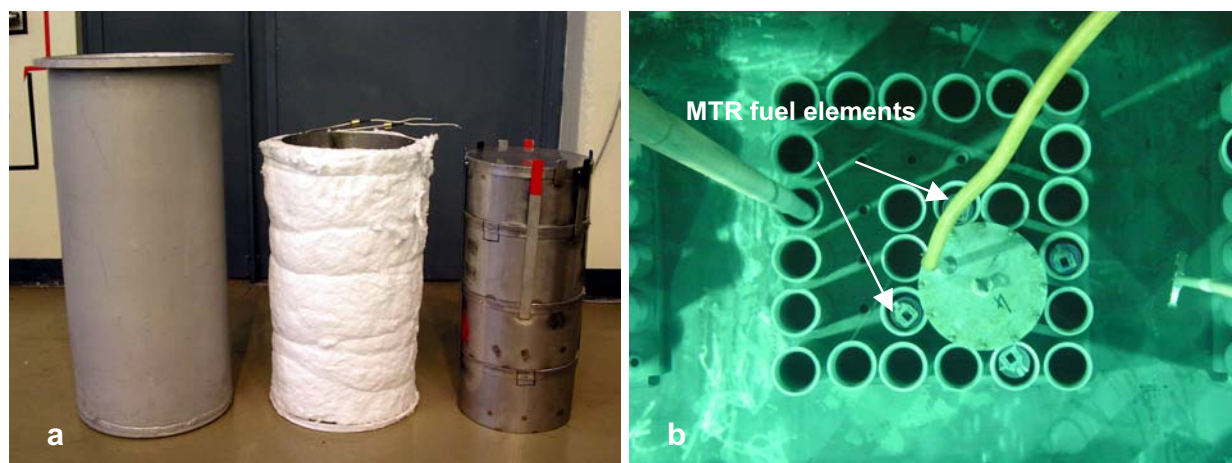


Figure 14. a – Outer container, heater, inner containers; b – Position of outer container in MTR cooling pool

The experiments with crushed materials lasted for 6 months. Sampling was performed every two months. The profile of dose rate at the place of container versus time is presented in Figure 15. The integral γ -dose over the period of 6 months amounted to approximately 5.3 MGy. In order to provide the same dose rate during the entire period, radiating elements were replaced by a fresh set after 78 days.

With intact material the experiments took about 23 days and the total absorbed dose amounted to ~ 1 MGy.

All experiments included blanks, which contained only the liquid phase and atmosphere (air, argon or oxygen).

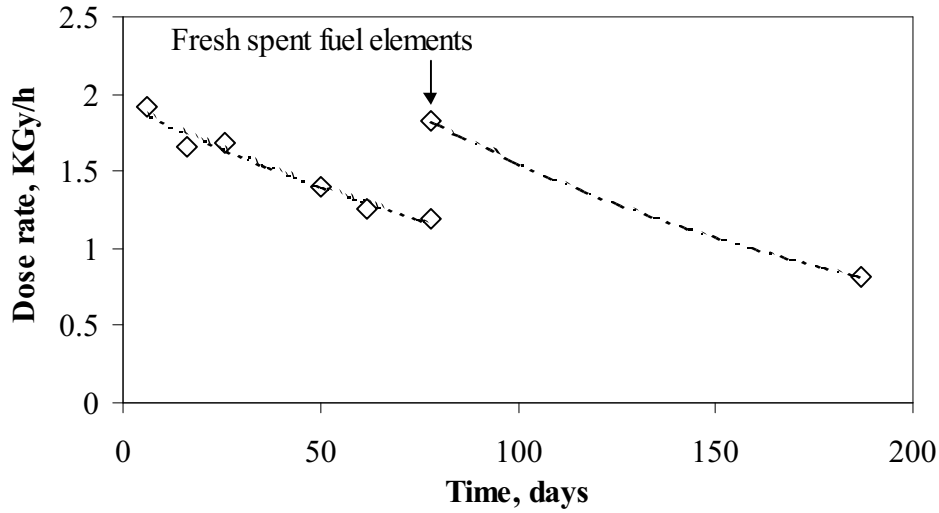


Figure 15. Dose rate in cooling pool versus time

C.3.2.1. Sampling procedure and calculation of amounts of graphite corroded

The gas phase in the tubes was analysed by gas chromatography. The glass tube was connected to a manometer and a gas mouse. Then the system was evacuated and flushed with argon several times. After final evacuation, the sealing of the vessel was broken by means of an iron ball, which was moved from the outside by a magnet (Figure 50 in Appendix). The gas was trapped in the gas mouse. The established equilibrium pressure after breaking the seal was measured and from this value the pressure in the sealed ampoule was calculated. The scheme of the sampling procedure is shown in Figure 50.

The calculation of reaction rates was performed assuming CO₂ equilibrium between aquatic and gas phases. To attain the equilibrium, the glass vessels were cooled down and maintained at room temperature for 4 hours before sampling.

The amount of CO₂ in the gas phase v_g (mol) is:

$$v_g = \frac{P_{CO_2} V_g}{RT} = \frac{P_0 X_{CO_2} V_g}{RT} \quad \text{Eq. (36)}$$

P_0 – total pressure in glass vessel (atm)

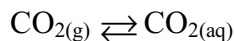
V_g – volume of gas phase in glass vessel (L)

X_{CO_2} – fraction of CO₂ in the gas phase (vol. %)

R – gas constant – 0.082 (L atm/(mol K))

T – temperature (K)

The equilibrium of CO₂ between the aqueous and gas phase is represented by the equation:



$$K = \frac{\gamma_{CO_2} [CO_2]}{p_{CO_2}} \quad \text{Eq. (37)}$$

where K is the thermodynamic constant for CO_2 at $25^\circ C$ $3.45 \cdot 10^{-2}$ (mol/(L atm)), [62] – the dissolved CO_2 concentration (mol/L), p_{CO_2} partial pressure of CO_2 (atm) in the gas phase and γ_{CO_2} the activity coefficient. In water $\gamma_{CO_2} = 1$.

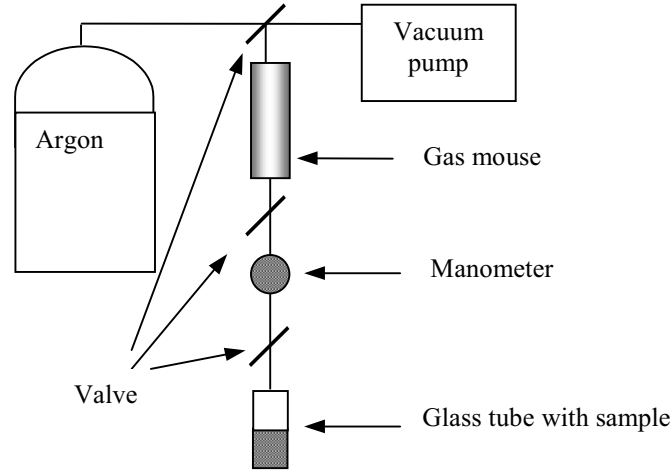


Figure 16. Sampling procedure

Activity coefficients γ_{CO_2} in brine-2 and brine-3 were calculated from the Pitzer specific interaction model and amounted to 7.36 and 3.24 respectively:

$$\ln \gamma_N = \sum_{c=1}^{N_c} m_c (2\lambda_{nc}) + \sum_{a=1}^{N_a} m_a (2\lambda_{na}) \quad \text{Eq. (38)}$$

m_c – the molality of cations

m_a – the molality of anions

N_c – the total number of cations

N_a – the total numbers of anions

λ_{na} and λ_{nc} – the parameter values for interactions CO_2 molecule – anion and CO_2 molecule – cation in the solution (Table 9 [62]).

λ_{na} The amount of CO_2 v_l in a liquid of volume V_l is:

$$v_l = \frac{p_{CO_2} K V_l}{\gamma_{CO_2}} \quad \text{Eq. (39)}$$

The total amount of CO_2 (mol) amounts to:

$$v_{tot} = v_g + v_l \quad \text{Eq. (40)}$$

The mass loss of carbon material m is:

$$m = \nu_{tot} \cdot M_C \quad \text{Eq. (41)}$$

where M_C – atomic weight of carbon, 12 g/mol.

Table 9. Composition of brines (molality) [61] and CO₂ – ion parameter values at 25°C [62]

Ion	Molality		$\lambda_{\text{CO}_2,i}$
	brine-2	brine-3	
Na	0.083	6.036	0.1
K	0.022	0.037	0.051
Mg	5.401	0.018	0.183
Ca	0.316	0.021	0.183
Cl	11.538	6.036	-0.005
SO ₄	0.0006	0.058	0.097

The corrosion rate R_{mv} [g/g·d] was determined as the mass loss of the sample from the initial sample mass m_0 for the period of time t as follows:

$$R_{mv} = \frac{m}{m_0 \cdot t} \quad \text{Eq. (42)}$$

The total uncertainty in the estimation of the corrosion rate R_{mv} was considered to be in the range of 30 %. It results from the sample preparation procedure and the precision of the gas chromatograph.

C.3.3. Thermal treatment of graphite

A scheme of the installation for graphite treatment is shown in Figure 18. It consisted of an argon flask, a flow controller, an evaporator, an oven with quartz reaction tube, 5 washing bottles and a CO–CO₂ IR detector. Before starting the experiment, the graphite sample was placed in a ceramic boat and weighed. Then the ceramic boat was pushed slowly into the quartz tube, which was placed in furnace, and heated up to the required temperature. The treatment was conducted in inert (argon) and oxidising atmosphere (water steam). The experimental details are listed in Table 10 and Table 11.

One experiment with the same sample of Merlin graphite was performed with water vapour pressure 70 kPa with stepwise increasing temperature (Table 12).

Table 10. Radioactive graphite treatment in argon atmosphere

Sample	Mass, g	T, °C	Time, hours	Flow rate, L/min
Merlin graphite bulk sample	1.3644	870	18	0.12
Merlin graphite powder	0.4023	970	9	0.12
Merlin graphite powder	0.15	1060	15	0.175
Merlin graphite bulk sample	0.9116	1060	13.5	0.12
AVR graphite	0.213	1060	15	0.08

Table 11. Radioactive graphite treatment in water steam atmosphere

Sample	Mass, g	T, °C	Time, hours	P _{H₂O} , kPa	Flow rate, L/min
Merlin graphite powder	0.439	1050	9.41	2.3	0.12
Merlin graphite bulk sample	0.446	1050	25.24	2.3	0.145
Merlin graphite powder	0.239	1060	11	7.4	0.66
Merlin graphite powder	0.2262	960	9.42	7.4	0.08
Merlin graphite powder	0.249	960	6.51	7.4	0.66
AVR graphite powder	0.087	1060	15.8	2.3	0.17
AVR graphite powder	0.0726	1070	13.1	31	0.17

Table 12. Oxidation of Merlin graphite powder

Sample	Mass, g	T, °C	Time, hours	P _{H₂O} , kPa	Flow rate, L/min
Merlin graphite powder	0.459	400	5	70	0.145
		600	5	70	0.145
		800	5	70	0.145
		955	5	70	0.145
		1055	5	70	0.145

Argon was flushed through the whole system. The carrier gas was saturated with water vapour by passing through an evaporator in the case of experiments with water steam oxidation. Volatile radionuclides were captured in washing bottles. The first washing bottle was filled with 40 mL 0.1 mol/l nitric acid. Tritium as HTO was absorbed in this bottle. After the first washing bottle, the concentration of CO and CO₂ in gas flow was detected by a CO–CO₂ analyser. Then the carrier gas was passed through the reactor tube with CuO at a temperature of 550°C in order to oxidise tritium, also present as triated molecular hydrogen in the gas mixture, and carbon monoxide to H₂O and CO₂, correspondingly. Oxidised molecular hydrogen was absorbed in the second and third bottles with 0.1 mol/L nitric acid. ¹⁴CO₂ passed through the first three bottles and was absorbed in the fourth and fifth washing bottles, which were filled with 40 mL 4 mol/L NaOH. The third and fifth bottles were set to check that all the tritium and ¹⁴C had been absorbed in the previous washing bottles.

The determination of the mass loss of the sample during the time was detected by the IR spectrometer from the CO and CO₂ concentration in the flow. Before every run the detector was calibrated by a calibration gas with a known concentration of CO and CO₂.

After the oven had been heated up to the proper temperature, samples of liquid phase 3 mL in the case of treatment of Merlin graphite and 1.5 mL in the case of AVR graphite were taken from the washing bottles at certain time intervals.

When the experiment was finished, the solutions in the washing bottles were replaced by fresh solutions and the graphite was burnt completely in oxygen atmosphere. Then the content of the washing bottles was analysed in order to determine the total amount of tritium and ¹⁴C in the graphite sample.

After complete combustion the ceramic boat was put into a beaker with 30 mL of hot concentrated HCl, heated for 2 hours and left for 24 hours. The liquid was evaporated up to dry residue and dissolved in 5 mL of 2 M HNO₃.

In order to determine the radionuclide transport during the treatment procedure, the reactor tube was divided into several sectors (sectors 1–4 Figure 17) and rinsed out step by step with concentrated HCl plus 1 mL of HF.

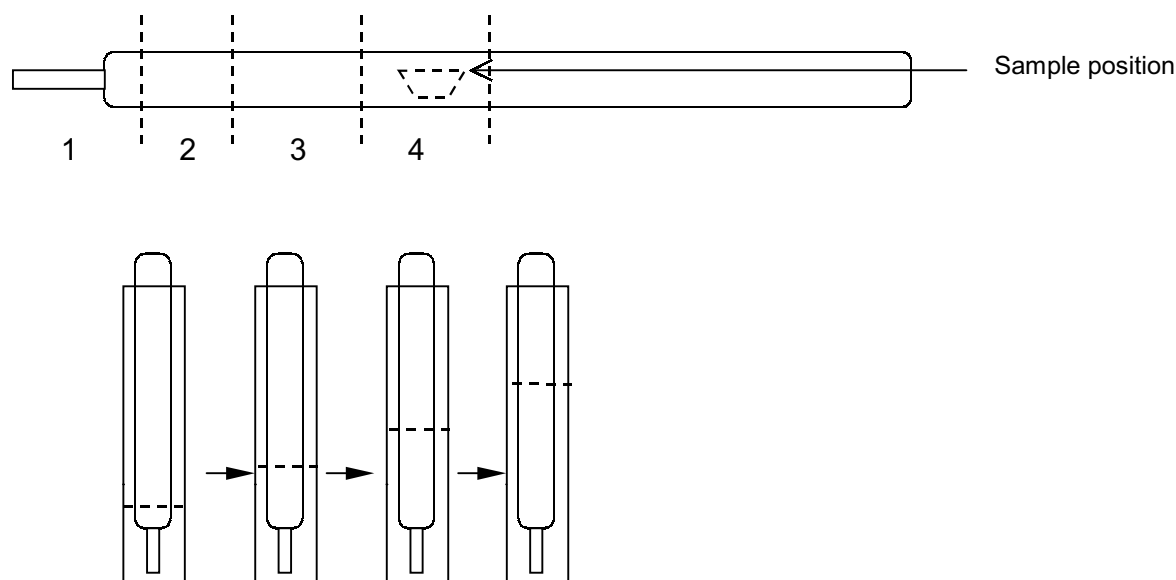


Figure 17. Washing procedure of reactor tube

Then the washing liquid was evaporated to dry residue and recovered with 5 mL of 2 M HNO_3 (the same procedure as with the boat).

Also after the washing procedure the reactor tube and the ceramic boat were analysed by γ -spectrometry in order to ensure that all the radioactivity had been removed.

Determination of ^3H

Tritium was retained in the three first bottles with 0.1 HNO_3 solution. In the experiments with Merlin graphite, an aliquot of 2 mL was mixed with 18 mL Instant Scint-Gel PlusTM and measured directly by LSC. In the experiments with AVR graphite, an aliquot 100 μL was taken from the bottles with HNO_3 mixed with 1.9 mL distilled water and 18 mL of Instant Scint-Gel PlusTM.

Determination of ^{14}C

An aliquot of 1 mL of solution was taken from the fourth and fifth washing bottles, mixed with 1 mL distilled water and 18 mL of HIONIC FLUORTM and measured directly with LSC.

Determination of total β, γ -activity

An aliquot of 100 μL from the dissolved residue was diluted with 1.9 mL H_2O and mixed with 18 mL of Instant Scint-Gel PlusTM and then measured directly by LSC.

Determination of γ -activity

An aliquot of 0.5 mL was taken from the solution of dissolved residue, diluted with 9.5 mL of H_2O in a plastic 10 mL bottle and measured with γ -spectrometry.

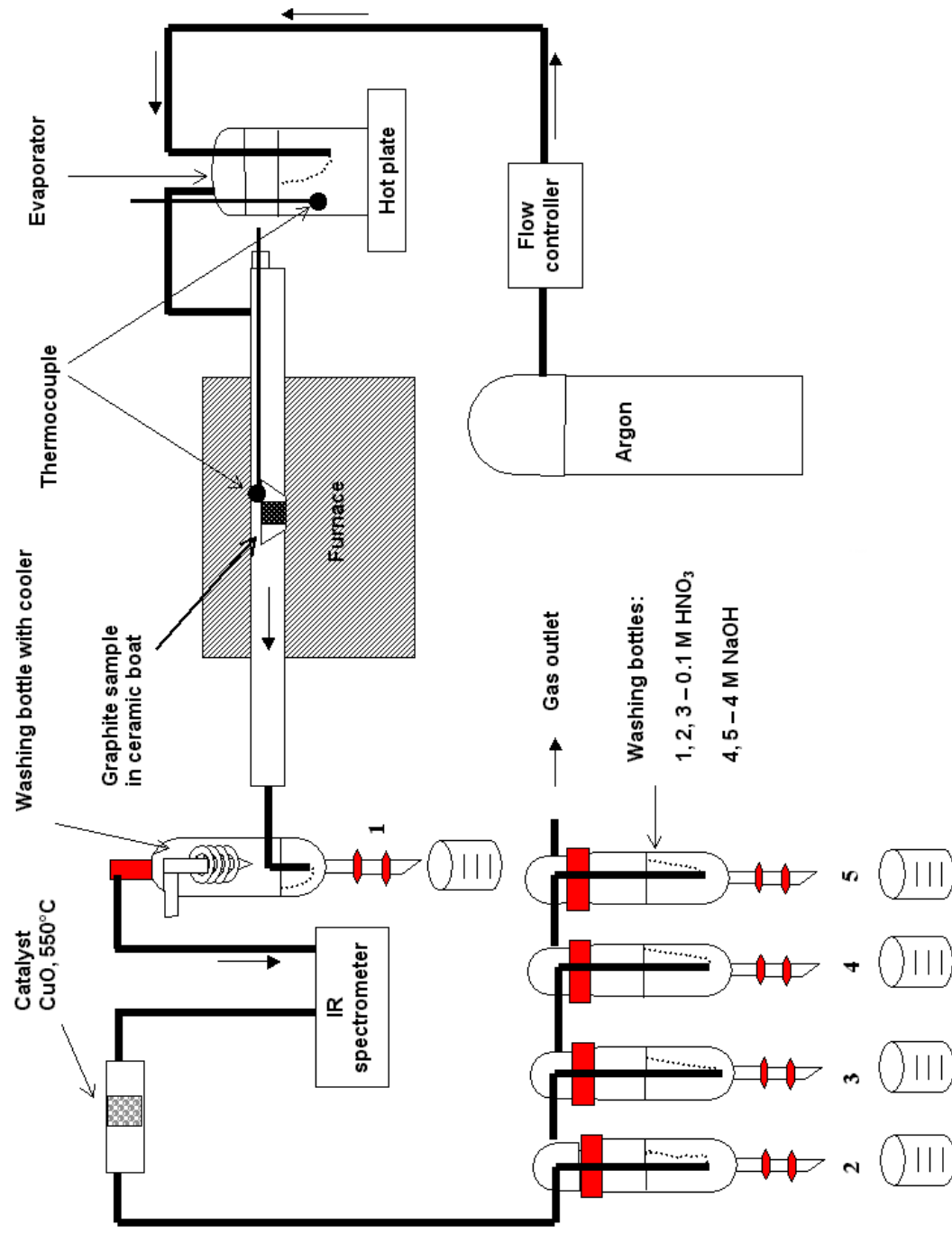


Figure 18. Installation for graphite thermal treatment

C.4. Characterisation of graphite and pyrocarbon materials

SEM investigation

The peculiarities of pyrocarbon and graphite morphology were investigated by SEM. Typical photographs of the cross section of fuel BISO and TRISO particles are presented in Figure 19. From the images obtained the mean thickness of the protective layers was determined. In the case of BISO particles, the outer pyrocarbon layer and buffer mean thickness amounts to $\sim 110\ \mu\text{m}$ and $55\ \mu\text{m}$, respectively. TRISO particles have four layers with the following mean thickness: outer pyrocarbon layer $\sim 35\ \mu\text{m}$, silicon carbide $\sim 25\ \mu\text{m}$, inner pyrocarbon $\sim 55\ \mu\text{m}$ and buffer $\sim 70\ \mu\text{m}$.

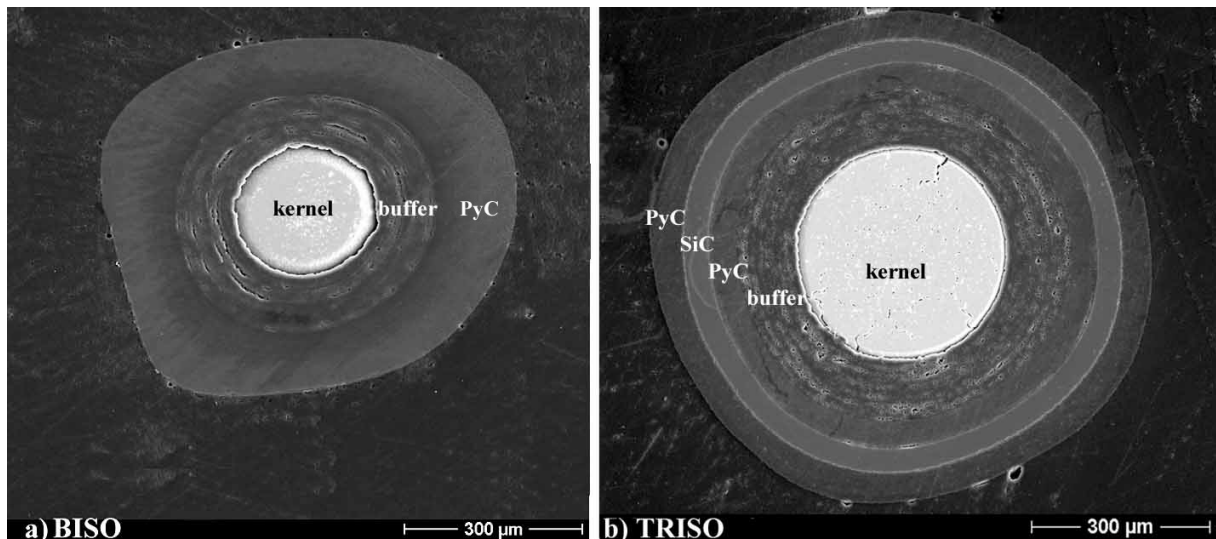


Figure 19. SEM images of cross section of BISO and TRISO particles

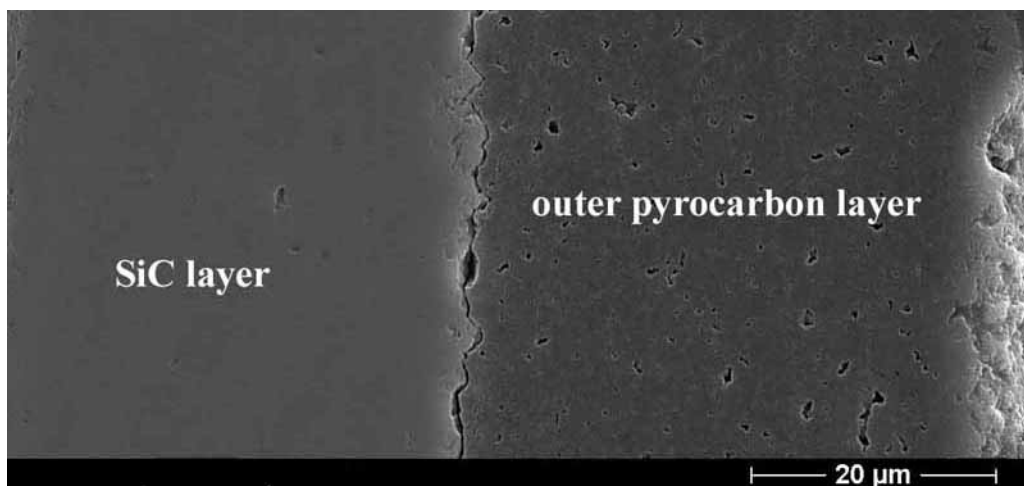


Figure 20. SEM image of cross section of TRISO particle: outer pyrocarbon layer and silicon carbide layer

The structure of the outer pyrocarbon layer is shown in Figure 20. One can see the difference in pore structure of pyrocarbon layer and silicon carbide coating. It can be seen that the pyrocarbon layer is rather dense and the maximum pore size is estimated to be about 1 μm .

The pore structure of the matrix graphite is shown in Figure 21. As can be seen, the matrix graphite has a well-developed pore structure in comparison with pyrocarbon.

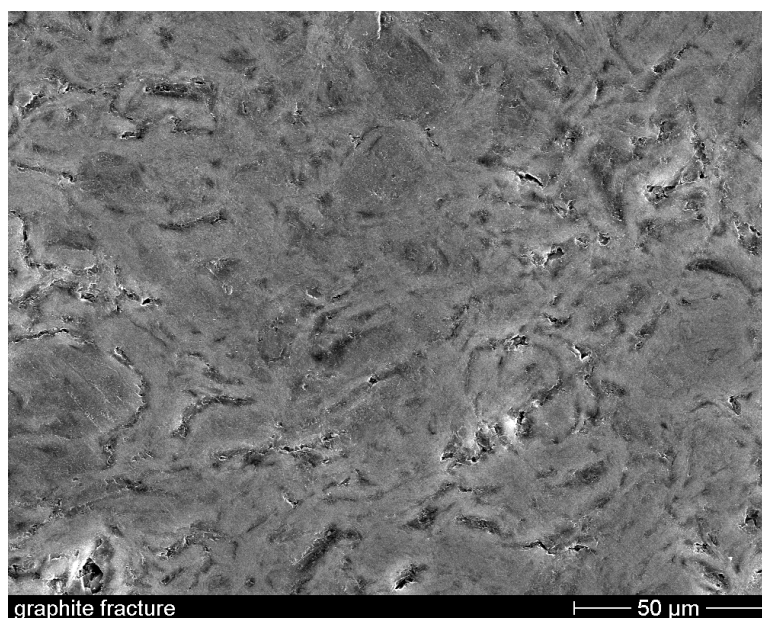


Figure 21. SEM image of matrix graphite section

The surface of particles from graphite powder and pyrocarbon coatings is presented in (Figure 22). The surface of the pyrocarbon is smooth and uniform, whereas the surface of the graphite powder is significantly rougher, and the graphite constituents can be clearly seen.

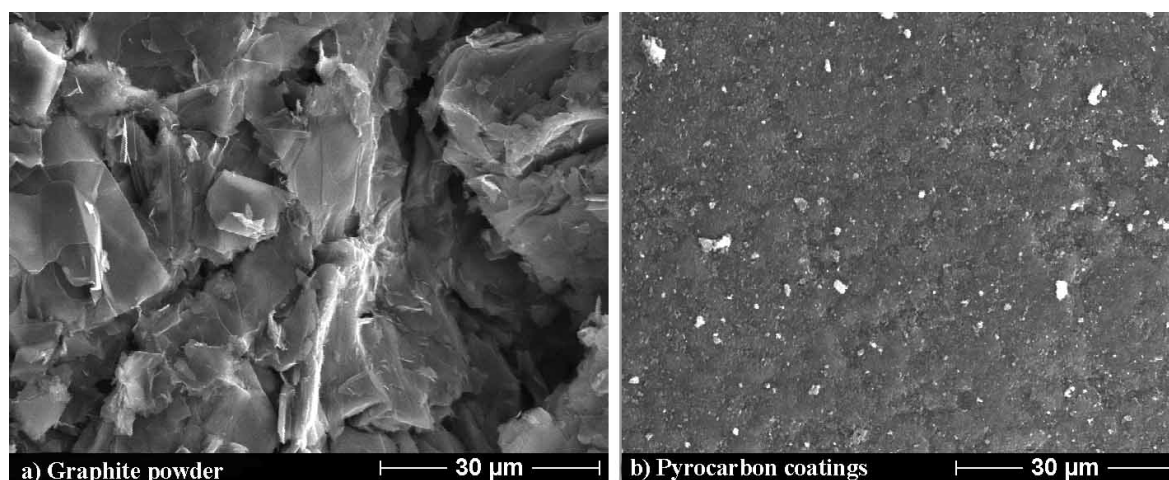


Figure 22. SEM images of graphite (a) and pyrocarbon surface (b)

XRD analysis

The investigated materials were studied by XRD. Characteristic spectra of graphite and pyrocarbon powders are presented in Figure 23 and listed in Table 13. From the position of

the 2θ angles it can be seen that the lines of graphite and pyrocarbon are in good agreement with the catalogue data [63]. A declination from intensity from catalog's value was observed. That can be caused by the worse crystallinity of the samples in comparison to catalog's data or by the graphite texture (the morphological peculiarities of the material part stacking).

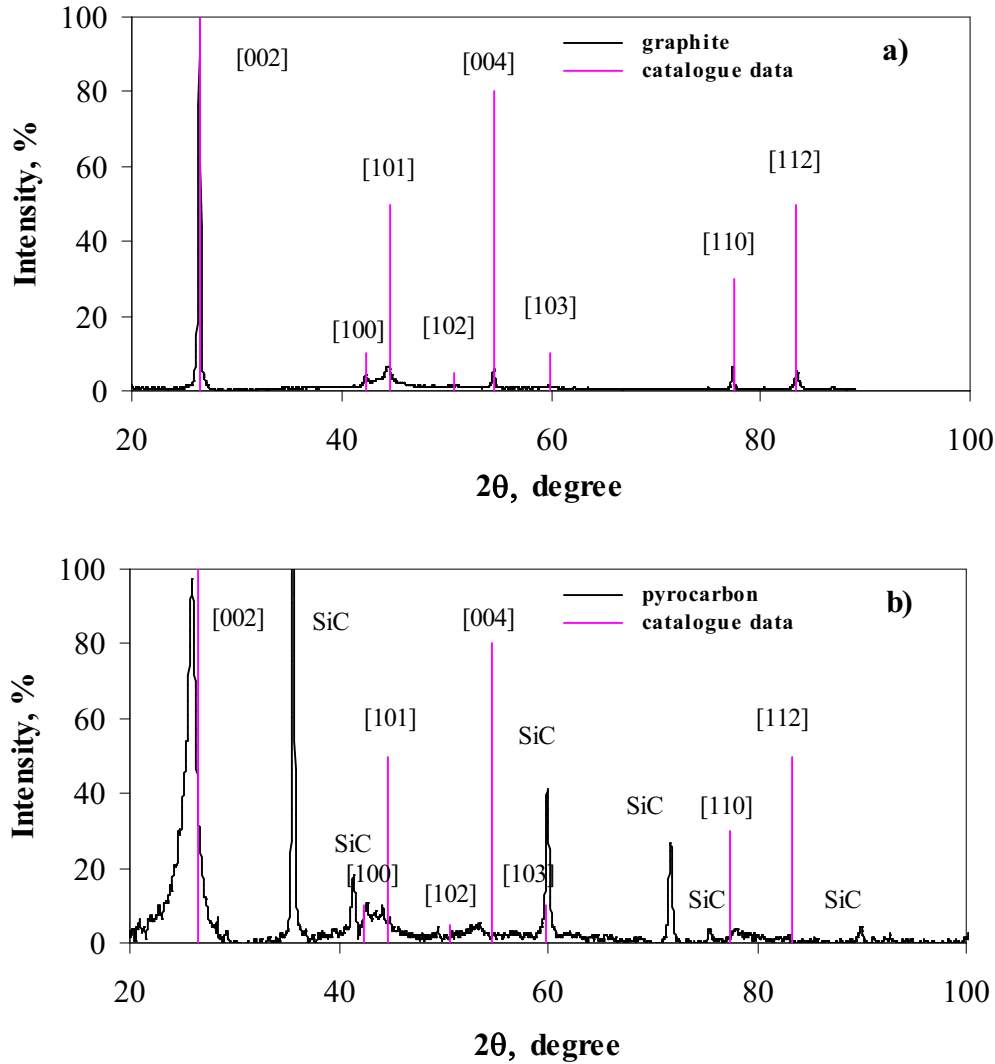


Figure 23. X-ray diffractogram of matrix graphite (a) and pyrocarbon coatings from TRISO particles (b)

In the spectrum of pyrocarbon obtained from TRISO coated particles besides the peak positions of the graphite lattice the signals from SiC are also present. In the case of pyrocarbon, broadening of the line (002) can be observed in comparison to the spectrum of matrix graphite. This can be referred to smaller crystallite size of pyrocarbon.

The crystallite size of both carbon materials can be estimated from the Scherrer equation [64]:

$$L = \frac{K_s \cdot \lambda}{B \cdot \cos \theta} \quad \text{Eq. (43)}$$

where K_s is 1.84 for two-dimensional peaks, and 0.89 for three-dimensional peaks, λ – the X-ray wavelength, B – is the broadening of diffraction line (full width at half maximum

intensity of the peak) at Braggs angle. Correction was performed for the instrumental resolution function.

The (002) reflection was used to estimate the carbon crystallite dimension perpendicular to the basal plane L_c , and the (110) reflection was used to estimate the crystallite dimension parallel to the basal plane, L_a .

Crystallite parameters L_a and L_c for graphite are 106 and 50 nm, respectively. The crystallite size of pyrocarbon is less and amounts to 5 nm – L_c and 21 nm L_a .

The difference in the crystallite size of matrix graphite and pyrocarbon is connected with the method of fabricating these materials.

Table 13. XRD data for pyrocarbon and matrix graphite

	hkl	002	100	101	102	004	103	110	112
pyrocarbon	2q,°	25.938	42.768	44.238		44.238	–	78.558	–
	I, %	100	11	9		4	–	3	–
graphite	2q,°	26.508	42.348	44.508	–	54.558	–	77.388	83.478
	I, %	100	3.8	5.8	–	5	–	5.7	4.5
catalogue data	2q,°	26.506	42.401	44.599	50.678	54.651	59.853	77.398	83.393
	I, %	100	10	50	5	80	10	30	50

BET and optical microscope investigations

The specific surface of graphite and pyrocarbon powder was determined by BET. Values for different graphite fraction and pyrocarbon coatings are given in Table 14.

Table 14. BET surface of investigated materials

Material	Fraction size, mm	S_{BET} , m ² /g	S_g , m ² /g
graphite >0.8 mm	>0.8	1.1	5.3E-03
graphite 0.5-0.8 mm	0.5-0.8	2.1	8.0E-03
graphite 0.15-0.25 mm	0.15-0.25	3.8	1.8E-02
graphite 0.05-0.15 mm	0.05-0.15	5.2	4.0E-02
graphite <0.05 mm	<0.05	4.8	2.0E-01
pyrocarbon	~0.4	2.1	8.0E-03

For optical microscope investigations the graphite powder was dispersed into a drop of oil over an object-plate. The microscope images of powder samples, each containing 500–1000 individual particles, were used to study the particle size distribution. They were analysed by image processing software. On the basis of this analysis, the specific geometric surface area was evaluated using the known powder density ρ :

$$S_g = \frac{6}{\rho \cdot d} \quad \text{Eq. (44)}$$

where ρ is the density of material (1.7 g/cm³ for graphite and 1.9 g/cm³ for pyrocarbon) and d is the effective particle diameter.

D. Results and discussion

D.1. Graphite corrosion in aqueous phase

D.1.1. Oxidation without γ -irradiation

Corrosion experiments in different aquatic phases under argon atmosphere without irradiation lasted over two years. After this time gas from the glass vessel was extracted by breaking the seal and analysed using gas chromatography. Negligible amounts of CO₂ were found in the gas phase in the range of 0.01–0.1 vol. % (Table 15). No carbon monoxide and hydrogen formation was detected. This indicates that corrosion was not caused by the interaction of graphite and water due to the reactions:



Therefore, the reaction of graphite with the trace amount of dissolved oxygen and oxygen absorbed on the surface was considered.

It can be seen in Table 15 that the quantity of CO₂ produced in the gas phase correlates with the specific surface area of different graphite fractions: the larger the graphite surface, the higher the CO₂ content was in the gas phase, which can be related to the amount of oxygen adsorbed on graphite.

Table 15. Gas composition of sealed tubes after experiments in argon atmosphere at 90°

Material	Solution	O ₂ , vol.%	N ₂ , vol.%	CO ₂ , vol.%	S, m ² /g	Time, days
graphite >0.8 mm	brine-2	n.d.	0.57	0.05	1.1	770
graphite 0.15-0.25 mm	brine-2	n.d.	0.78	0.12	3.9	770
graphite 0.05-0.15 mm	brine-2	0.15	0.74	0.16	5.2	770
graphite <0.05 mm	brine-2	n.d.	0.36	0.20	4.8	790
pyrocarbon	brine-2	0.26	0.98	0.01	2.1	249
pyrocarbon	brine-2	0.21	0.91	0.04	2.1	249
pyrocarbon	brine-2	n.d.	n.d.	0.11	2.1	249
graphite <0.05 mm	water	0.18	1.15	0.10	4.8	137

In order to investigate the influence of dissolved oxygen on the graphite corrosion rate, additional short term experiments were performed under pure oxygen and air atmosphere. Besides CO₂, small concentrations of carbon monoxide were found under these conditions as a reaction product. As in the experiments under argon atmosphere, hydrogen was not detected in the system either. Results of gas phase analysis are presented in Table 28 (appendix). Switching from argon to oxidising atmosphere leads to an increase in corrosion rates. Comparison of corrosion rates in oxygen and air atmosphere gives a difference of factor two for all liquid phases used. The dependence of the average corrosion rate of graphite in logarithmic scale versus time is presented in Figure 24. It can be seen that under oxygen and air atmosphere the average corrosion rate was approximately constant during the whole period of the experiment.

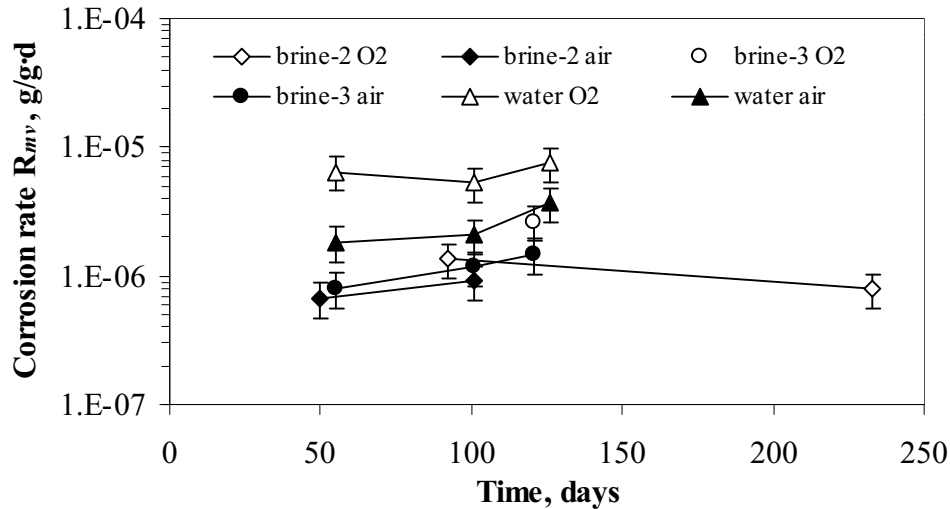


Figure 24. Corrosion rates of graphite in different aqueous solutions in oxidising atmosphere

As can be seen from the Figure 24, the corrosion rate of graphite in water is higher than in concentrated saline brines. The corrosion of carbonaceous materials can be explained by interaction with dissolved molecular oxygen. As is known, the solubility of gases in salt solution differs from their solubility in pure water and can be described using the equation

$$\ln\left(\frac{S_0}{S}\right) = \ln \gamma \quad \text{Eq. (47)}$$

where S is the molal gas solubility in pure water (S^0) and in solution (S), γ is the corresponding activity coefficient of dissolved gas, which is a function of the concentration of all solute species. In concentrated chloride solution NaCl and MgCl₂, the solubility of oxygen decreases with increasing salt concentration and temperature [65, 66].

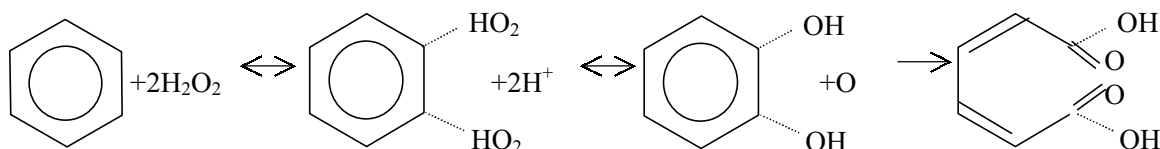
In the literature there is a lack of information about graphite oxidation in the liquid phase. Graphite corrosion was investigated in water under air atmosphere at high temperature (200, 250, 300°C) by Gray [45, 51]. The corrosion rate at 99°C was obtained by extrapolation. It amounted to $2.4 \cdot 10^{-5}$ g/(g·d). The average corrosion rate of graphite obtained in the present work was $2 \cdot 10^{-6}$ g/(g·d) for the experimental conditions “water-air atmosphere-90°C”.

D.1.2. Graphite oxidation with hydrogen peroxide

The influence of oxidant concentration in the liquid phase was investigated by experiments simulating the water radiolysis effect. Hydrogen peroxide is one of the most stable species produced during water radiolysis and can remain in liquid phase for a long time. The results of the oxidation experiments with water and brine-2 containing H₂O₂ in different concentrations are shown in Figure 25. In the composition of the gas phase carbon dioxide and a lower amount of carbon monoxide were determined as products of carbon corrosion and a significant amount of oxygen as a result of H₂O₂ decomposition (Table 29 in appendix).

Carbon can react as a catalyst to decompose hydrogen peroxide. The mechanism of carbon oxidation with hydrogen peroxide described in [67] assumes that hydrogen peroxide molecules react with the graphite surface with formation of active atomic oxygen. This oxygen can move to another site on the surface, where it is adsorbed until it recombine with

another oxygen atom and forms O_2 gas, or atomic oxygen can be added to the surface carbon in the aromatic ring to form a $>C=O$ group:



If this oxidation mechanism takes place on adjacent carbon atoms in the aromatic ring, as is shown, the aromatic ring will be damaged.

In the case of experiments with distilled water, the graphite corrosion rate was one order of magnitude higher than in brine-2. The decrease of the corrosion rate in chloride media can be attributed to scavenging of hydrogen peroxide by Cl^- ions because in KCl or NaCl saturated solutions H_2O_2 is decomposed to water and molecular hydrogen [15].

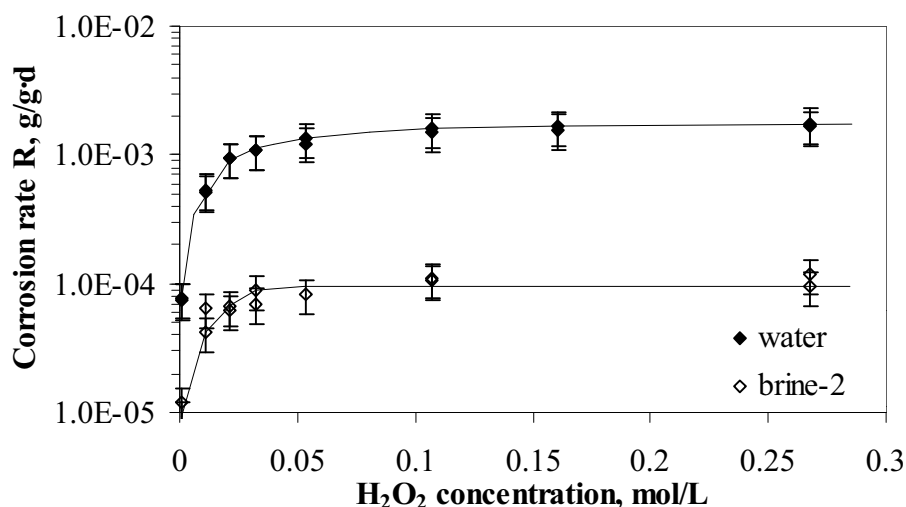


Figure 25. Graphite corrosion rate in distilled water and brine-2 containing H_2O_2

It can be seen from Figure 25 that the dependence of the graphite corrosion rate on hydrogen peroxide concentration does not have a linear character. In water the graphite oxidation rate hardly depends on hydrogen peroxide concentration, when the latter is higher than 0.1 mol/L and in brine higher than 0.03 mol/L. The possible reason is that hydrogen peroxide decomposition is proportional to its concentration [68] and at higher concentrations the reaction of H_2O_2 with the graphite surface will compete with the reaction with other peroxide molecules, leading to its decomposition.

The steady state concentration of H_2O_2 in argon and oxygen-purged water reported by Christensen and Sunder [59, 69] amounts to $3.9 \cdot 10^{-8}$ mol/L and to $3.4 \cdot 10^{-4}$ mol/L, respectively, at a dose rate of 280 Gy/h. The concentration range of our experiments was conservative with respect to this value, because the CO_2 concentration in gas phase was below the detection limit in the case of oxidant concentrations lower than 10^{-3} mol/L. The approximation of the steady state concentration of H_2O_2 as $3.9 \cdot 10^{-8}$ mol/L, and considering that H_2O_2 will be the main oxidant in irradiated solutions, gives a value of the graphite corrosion rate similar to that under the argon atmosphere ($\sim 10^{-8}$ g/(g·d)). This means that at

low irradiation dose in the absence of oxygen in the system, which corresponds to final repository conditions, hydrogen peroxide will not have a significant influence on pyrocarbon and graphite corrosion.

D.1.3. Graphite and pyrocarbon oxidation in the presence of γ -irradiation field

In order to study the influence of water radiolysis on graphite and pyrocarbon corrosion, experiments were performed in the presence of γ -irradiation source in the MTR cooling pool. It should be noted that the irradiation dose absorbed by samples was conservative with respect to repository relevant conditions. The gas phase composition of reaction vessels is presented in Table 30, Table 31 and Table 32. The main gas products in brine-2 and brine-3 were CO_2 , H_2 and O_2 . Also small amounts of CO were found. As can be seen from the results, irradiation of the doses used dramatically influenced the corrosion rate of carbonaceous materials in the chloride brine media. The level of CO_2 in the gas phase in experiments with brines was in the range of 17 vol. % after 2 months and increased up to 25 vol. % after 6 months. For comparison, the CO_2 production in corrosion experiments under oxygen atmosphere in the absence of irradiation field was about 0.1 vol. %.

The fraction of oxidised carbon increases with increasing adsorbed dose (Figure 26). As can be seen, the dependence of the evolved amount of CO_2 on the adsorbed irradiation dose has a linear character for the brine-2 and brine-3 series. The CO_2 production was not very high and amounted to 0.13 – 0.65 vol. % in experiments, where water was used as the aqueous media. No visible tendency to increase the amount of oxidised graphite with adsorbed irradiation dose was revealed.

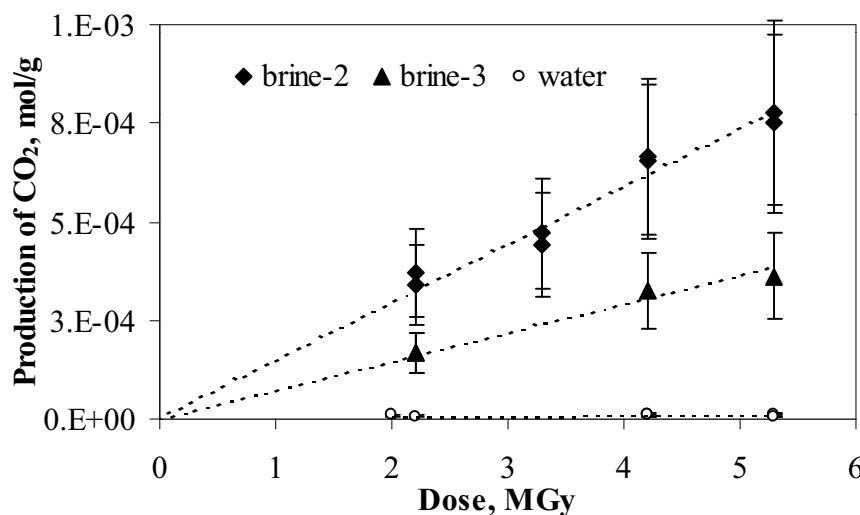


Figure 26. The amount of CO_2 produced during irradiation in brine-2 and brine-3.

Molecular hydrogen and oxygen were produced due to water radiolysis. Equilibrium concentrations of H_2 , generated in water, are small [59]. Thus the equilibrium of H_2 pressure in the gas phase was also small – about 2 vol. % Table 31. The only species, which can react with the hydrogen molecule, is the OH radical. In brines, OH radicals are scavenged with Cl^- ions, which leads to the increase of hydrogen production, and hydrogen content in experiments with brine-2 and brine-3 was on average 40 vol. %. The composition of the gas

phase above the solution in the experiments with water and brines is presented graphically in Figure 27.

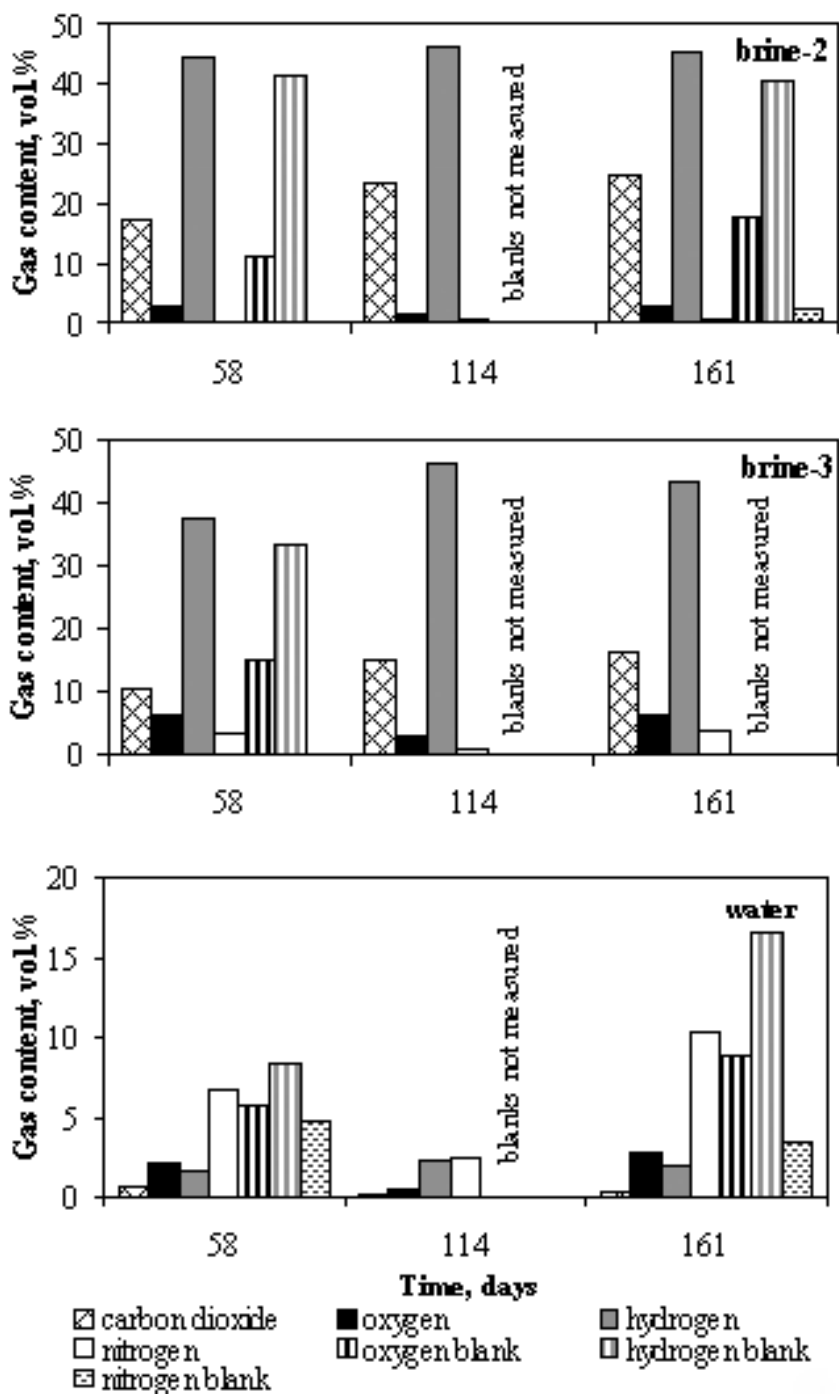


Figure 27. Gas composition of sealed tubes in irradiation experiments vs. time in brines and water

The formation of molecular oxygen in blanks of all aqueous phases is higher than in the presence of graphite. Oxygen can be consumed in reaction with graphite. Also oxygen is formed in water radiolysis due to reactions:





$\text{OH}\cdot$ and $\text{HO}_2\cdot$ are oxidising species which can take part in graphite oxidation. In the presence of graphite they will be consumed by the reaction with the graphite surface which causes a decrease in O_2 production.

Graphite and pyrocarbon corrosion rates under γ -irradiation in comparison with other experiments are listed in Table 16.

Table 16. Pyrocarbon and graphite mean corrosion rates under different conditions

Material	Aqueous solution	Atmosphere	γ -irradiation	R_{mv} , g/g·d
graphite	brine-2	oxygen	–	1.1E-06
graphite	brine-3	oxygen	–	3.0E-06
graphite	water	oxygen	–	6.6E-06
graphite	brine-2	air	–	7.9E-07
graphite	brine-3	air	–	1.2E-06
graphite	water	air	–	2.5E-06
graphite	brine-2	argon	+	6.2E-05
graphite	brine-3	argon	+	3.2E-05
graphite	water	argon	+	1.1E-06
pyrocarbon	brine-2	oxygen	–	1.9E-07
pyrocarbon	water	oxygen	–	9.6E-07
pyrocarbon	water	air	–	7.0E-07
pyrocarbon	brine-2	air	–	4.4E-07
pyrocarbon	brine-2	argon	+	2.6E-05
pyrocarbon	water	argon	+	1.3E-06

Results showed that in brines corrosion was much faster under irradiation. The corrosion rate amounted to $\sim 6 \cdot 10^{-5}$ g/(g · d) and $3 \cdot 10^{-5}$ g/(g · d) in brine-2 and brine-3 in argon atmosphere under γ -irradiation, respectively. As can be seen from the results of experiments under pure oxygen atmosphere, such significant increase of corrosion rate can not be caused only by oxygen produced by water radiolysis but mainly by other oxidising species. From the literature it is known that under γ -irradiation in high molar chloride solutions formation of chlorate and hypochlorite takes place [57, 58, 70]. The concentration of chlorate in 6 mol NaCl solution, reported by Kelm [58], is about 10 mmol/kg after γ -irradiation with total adsorbed dose ~ 1 MGy. The concentration of hypochlorite in 6 M NaCl in steady state can reach a micromolar level. Redox potentials of chlorate and hypochlorite acid in acid solutions are $E^0 = 1.49$ V and $E^0 = 1.5$ V, respectively:



After irradiation the Eh potential of aqueous phases was measured. For brine-2 it amounted to 950 mV and for brine-3 500 mV. Fresh unirradiated solutions gave a value of 450 mV and 150 mV, respectively. Thus it can be considered that aqueous media became more oxidising in comparison with initial conditions. This explains the increase of the graphite corrosion rate in saline brines under γ -irradiation.

For all the experimental time, a constant average rate of the graphite corrosion was observed for brine-2 and brine-3 (Figure 28).

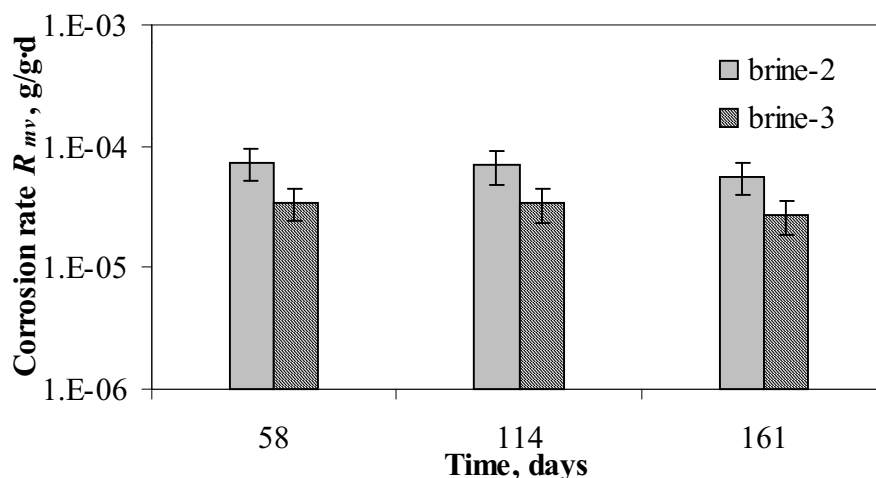


Figure 28. Graphite corrosion rate under gamma irradiation in brines vs. time

In water, graphite and pyrocarbon corrosion rate was lower under γ -irradiation than in experiments with oxygen and air atmosphere and amounted to 10^{-6} g/(g · d). The oxidation of carbon materials in this case is caused by oxygen and hydrogen peroxide formed in the system due to water radiolysis. The oxygen content in the gas phases was 0.3–3.0 vol. %, which is less than in experiments performed under oxidising atmosphere.

After the experiments in the reactor cooling pool, the surface of a bulk graphite sample and coated particles was investigated by SEM. Representative images from the samples before and after irradiation in brine-2 are presented in Figure 29 and Figure 30c, f. Changes in the surface structure can be observed. The corrosion leads to almost uniform surface etching, which becomes apparent in a more developed surface roughness.

No visible changes of the material surface were observed during irradiation in water (Figure 30b, e)

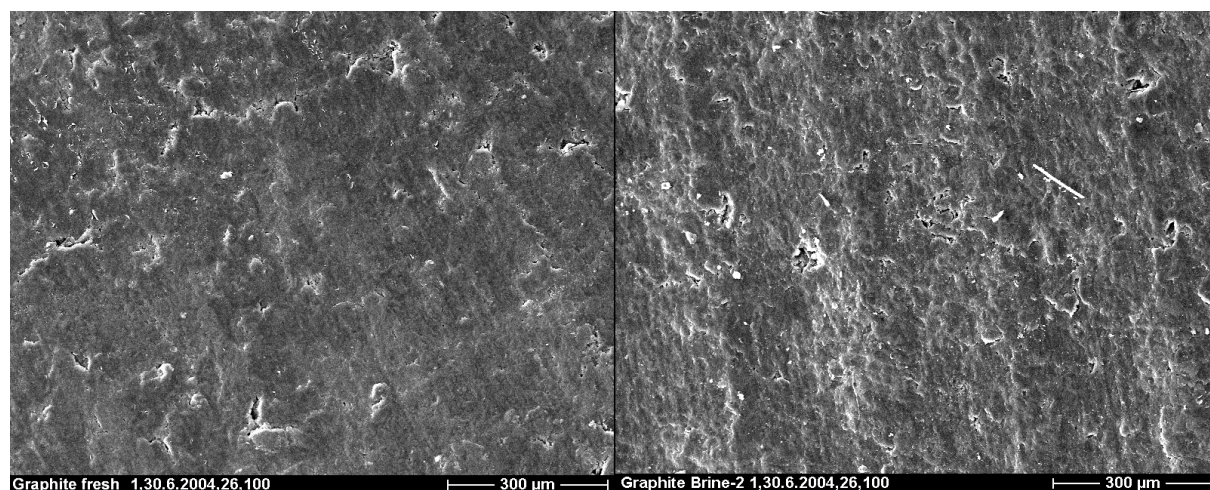


Figure 29. SEM images of graphite surface before and after γ -irradiation

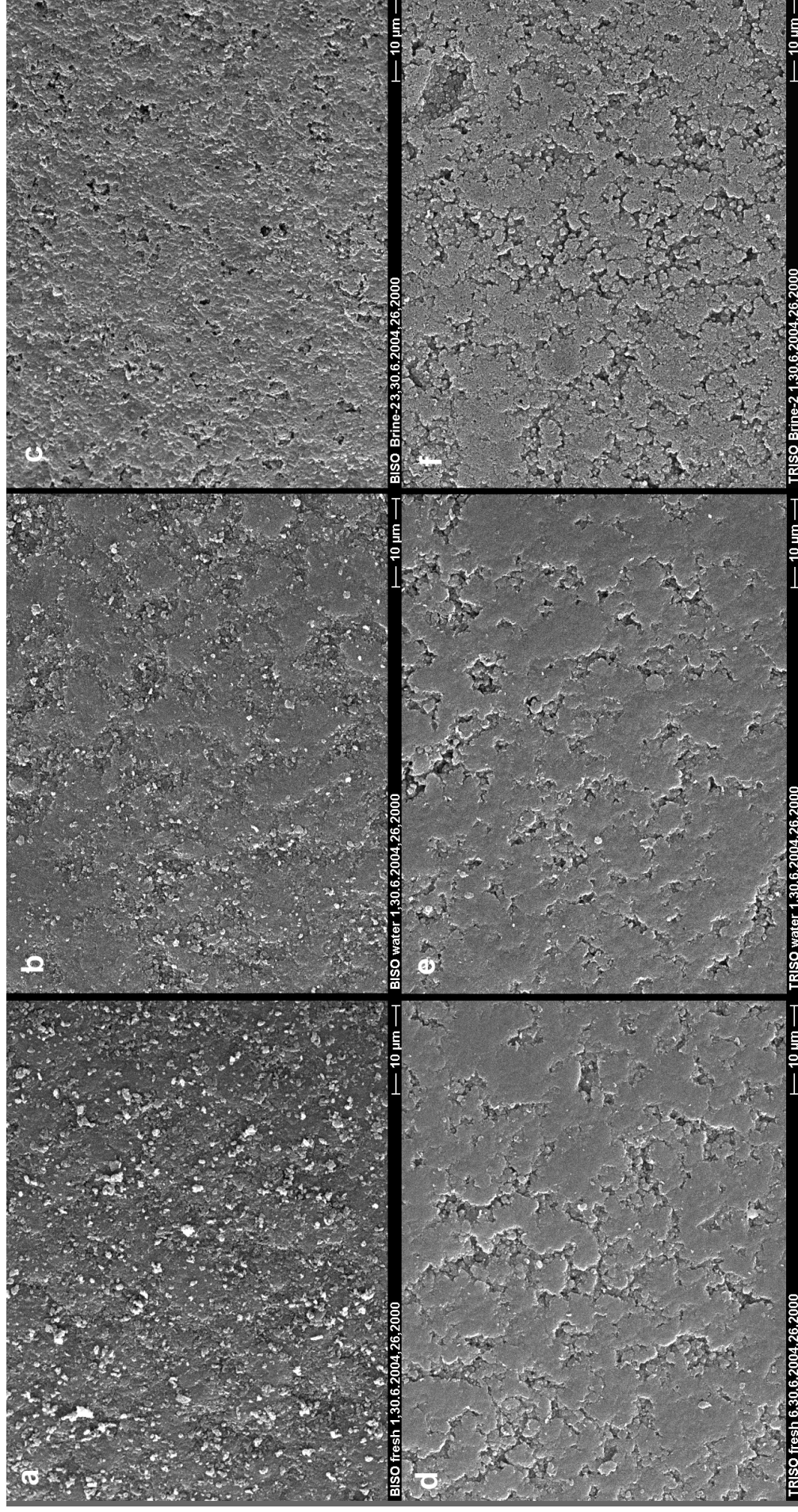


Figure 30. SEM images of BISO (a, b, c) and TRISO particles (d, e, f) before (a, d) and after γ -irradiation in water (b, e) and brine-2 (c, f)

The surface of carbon materials was investigated by EDX analysis. This was done in order to exclude the possibility of salt deposition. The elemental analysis showed the absence of sodium and magnesium chloride on the carbon surface. Therefore a change in surface profile can be related to the corrosion process. In pure water no significant changes of graphite oxidation were revealed nor any pressure increase. The graphite surface appearance after an experiment in water was identical to that before irradiation in γ -field.

It was also reported by Gray [45] that radiation caused no measurable effect on graphite corrosion in water at temperature about 30°C. In this case, however, experimental time was rather short – 24 hours, thus it can be supposed that corrosion, caused by irradiation of water, is rather slow and can not be detected after such a short time.

D.1.4. The lifetime estimation of pyrocarbon coatings and graphite protective layer

The protective properties of covering layers are typically characterised by their lifetime in contact with aquatic phases. Usually the term lifetime is considered as the time until the protective layer is totally corroded. In the present work two different models of material corrosion were considered for lifetime estimation: uniform surface corrosion and bulk corrosion of porous materials.

The simple model of uniform surface corrosion implies the continuous dissolution of an infinite layer in the direction normal to its surface. The corrosion rate R_s (g/m²·d), used for such estimations, is normalised to the surface area of sample in oxidation experiments in aqueous phases. If the protective layer has the known thickness d , the lifetime of the protective layer can be estimated from the mass balance as:

$$\tau = \frac{d\rho}{R_s} \quad \text{Eq. (52)}$$

where ρ – density. The corrosion rate can be calculated from the results of oxidation experiments in aqueous phases by the following formula:

$$R_s = \frac{m_c}{S \cdot t} \quad \text{Eq. (53)}$$

where m_c is the mass of material (g) corroded during the time interval t (d), and S is the surface area of sample (m²). The principle of m_c calculation can be found in Chapter C.3.2.1.

The surface area of sample in oxidation experiments used for corrosion rate determination is usually estimated either by a geometrical method or BET measurements. The latter method considers the total material surface available, which is significantly higher than the surface area undergoing corrosion. Therefore, the BET surface of samples is often overestimated, resulting in a consequent overestimation of the layer lifetime.

Further, the terms R_{sg} and R_{SBET} will be used for corrosion rates normalised to geometrical and BET surface areas, respectively. The corresponding lifetimes, calculated by Eq. (52), will be denoted as τ_g and τ_{BET} .

The above considerations assume surface corrosion. However, for materials possessing an open porous system the penetration of aquatic phase inside the material will lead to a different corrosion mechanism – bulk corrosion. In this case, the corrosion takes place through the whole material volume simultaneously, and the influence of the outer surface area becomes

negligible. If one considers the bulk corrosion of sample, the mass balance of uniform corrosion will be:

$$m = \tau_v S' R'_S \quad \text{Eq. (54)}$$

where τ_v – the time for which the sample of mass m will be corroded, S' is the surface area of pore system in the sample, and the surface area normalised corrosion rate is:

$$R'_S = \frac{m_c}{t \cdot S'} \quad \text{Eq. (55)}$$

Combining Eq. (54) and Eq. (55), the given mass balance is reduced to:

$$\tau_v \left(\frac{m_c}{t \cdot m} \right) = 1 \quad \text{Eq. (56)}$$

The value in brackets represents the corrosion rate R_{mv} [g/g · d] normalised to the sample mass:

$$R_{mv} = \frac{m_c}{t \cdot m} \quad \text{Eq. (42)}$$

Therefore, the lifetime in the case of bulk corrosion is independent of the sample size and is determined mainly by the pore system morphology:

$$\tau_v = \frac{1}{R_{mv}} \quad \text{Eq. (57)}$$

The mean corrosion rates with different normalisation used for estimating graphite and pyrocarbon lifetime are shown in Table 17 and Table 18 respectively.

Table 17. Mean corrosion rates of graphite

Solution	Atmosphere	Irradiation	R_{Sg}, g/m²·d	R_{SBET}, g/m²·d	R_{mv}, g/g·d
brine-2	oxygen	–	5.4E-06	2.2E-07	1.1E-06
brine-3	oxygen	–	1.5E-05	6.3E-07	3.0E-06
water	oxygen	–	3.1E-05	1.3E-06	6.2E-06
brine-2	air	–	9.6E-06	1.8E-07	7.9E-07
brine-3	air	–	1.9E-05	2.8E-07	1.2E-06
water	air	–	2.7E-05	5.7E-07	2.5E-06
brine-2	argon	+	5.1E-04	1.3E-05	6.7E-05
brine-3	argon	+	2.5E-04	6.2E-06	3.2E-05
water	argon	+	8.6E-06	2.2E-07	1.1E-06

Table 18. Mean corrosion rates of pyrocarbon

Particle type	Solution	Atmosphere	Irradiation	R_{sg} , g/m ² ·d	R_{SBET} , g/m ² ·d
powder	brine-2	oxygen	–	2.4E-05	9.4E-08
powder	water	oxygen	–	1.2E-04	4.8E-07
powder	brine-2	air	–	5.7E-05	2.2E-07
powder	water	air	–	8.9E-05	3.5E-07
powder	brine-2	argon	+	6.7E-03	2.6E-05
powder	water	argon	+	3.0E-04	1.2E-06
TRISO*	brine-2	argon	+	3.6E-02	–
BISO*	brine-2	argon	+	2.8E-02	–

* – experiments with intact particles

Lifetime of graphite

The τ_g and τ_{BET} of the matrix graphite layer of 5 mm were calculated from the experiments with powders and presented in Table 20. The geometrical surface area of graphite powders was calculated from optical microscope investigations and listed in (Table 14).

The graphite layer lifetime estimated in this way does not take into account the porous system of the investigated materials. According to SEM investigations, graphite has an open pore system (Figure 21) and the water phase can penetrate inside the graphite matrix. The fact that graphite possesses an open porosity can be proved from the diffusion experiments performed with the matrix graphite discs [71]. In these experiments the migration of radionuclides through the graphite layer of 1 cm was observed. Other evidence of penetration of aqueous phase into the graphite pore system results from EDX investigation of graphite pellets wetted in MgCl₂-rich solution. The presence of Cl inside the graphite was observed after crushing the pellets and investigating the break surface.

Comparing the results of corrosion under γ -irradiation in the MTR cooling pool obtained for bulk and powder samples, it can be seen that for the same period of time the equal fraction of the material is consumed from the bulk sample as well as from the graphite powder, despite a higher specific surface area determined by BET for powder (Table 19). This can be explained by the fact that water can penetrate through the pore system and cause corrosion from inside. In this case, the corrosion rate of graphite will be determined mainly by the constitution size of matrix graphite, namely, by the size of the grains (<100 μ m [72]). Consequently, the lifetime of the whole matrix will be equal to the lifetime of graphite grains. The reactivity of grains will in turn depend on the amount of the accessible active sites responsible for carbon oxidation reaction with liquid and gases [3, 73, 74].

From the consideration given above, the lifetime of graphite layer was also calculated using the second approach for lifetime estimation taking into account the volume corrosion. The lifetimes estimated for surface corrosion of graphite pebble (τ_g and τ_{BET}) and for the assumption of penetration of aqueous phase inside the pore system (τ_v) are presented in Table 20.

Table 19. Graphite in aqueous solutions under γ -irradiation

Sample	Aqueous phase	Time, day	Sample mass, g	CO ₂ , mol/g
graphite massive	brine-2	56	0.1060	4.20E-04
graphite massive	water	56	0.2085	1.74E-05
graphite powder	brine-2	58	1	3.50E-04
graphite powder	water	58	1	8.00E-06

Table 20. Lifetime of graphite under different conditions

Solution	Atmosphere	Irradiation	τ_g , years	τ_{BET} , years	τ_v , years
brine-2	oxygen	–	4.7E+06	1.1E+08	2.8E+03
brine-3	oxygen	–	1.5E+06	3.7E+07	9.0E+02
water	oxygen	–	7.6E+05	1.8E+07	4.5E+02
brine-2	air	–	3.2E+06	1.4E+08	3.9E+03
brine-3	air	–	1.7E+06	8.7E+07	2.5E+03
water	air	–	1.4E+06	4.5E+07	1.2E+03
brine-2	argon	+	4.6E+04	1.8E+06	4.6E+01
brine-3	argon	+	9.5E+04	3.8E+06	8.5E+01
water	argon	+	3.4E+06	1.3E+08	3.0E+03

Lifetime of pyrocarbon

As is known the pyrocarbon is a very dense material [23, 24] The pyrocarbon pore structure is shown in Figure 22. The first approach considering uniform corrosion from the geometrical surface was applied for the calculation of lifetime. The results of these calculations are listed in Table 21. In the case of the experiments with intact coated particles performed in the presence of γ -irradiation, the corrosion rate R_{Sg} was normalised to the geometrical surface of the particles. In the experiments with pyrocarbon powder, the geometrical surface of the powder was calculated from optical microscope investigations and amounted to 0.008 m²/g. It can be seen from Table 21 that τ_g estimated from the experiments with powder and intact particles is in the same order of magnitude. This proves our consideration about material corrosion from the external geometrical surface in the case of particles.

Life times τ_g and τ_{BET} can be considered as lower and upper limit estimations. In the case of graphite, however, the possibility of water phase penetration inside the porous system of graphite matrix also should be taken into account. Therefore the lower limit estimation of graphite lifetime will be τ_v .

As can be seen from Table 21 and Table 20 γ -irradiation diminishes the lifetime of the protective matrix graphite and pyrocarbon layers by approximately two orders of magnitude. However, the irradiation dose used in the present study was extremely conservative with respect to final repository conditions. The γ -irradiation dose rate calculated for different types of spherical fuel elements after 200 days of cooling time is in the range of 17–55 Gy/hour for one element [75], whereas in the present study the irradiation dose rate was about 2 kGy/hour. As was shown above, the corrosion rate depends on the concentration of reactive species which are formed during the irradiation of liquid phase. The concentration of these species is proportional to the irradiation dose rate [59]. Therefore it can be argued that the lifetime of graphite and pyrocarbon coating will be much higher than that calculated above.

The presence of air atmosphere in the final repository also seems to be unlikely because all oxygen will be consumed in the first short period of time due to corrosion of storage cask [75].

Table 21. Lifetime of pyrocarbon under different conditions

Particle type	Solution	Atmosphere	Irradiation	τ_g , years	τ_{BET} , years
BISO	brine-2	oxygen	–	2.3E+04	5.3E+06
BISO	water	oxygen	–	4.6E+03	1.0E+06
BISO	brine-2	air	–	1.0E+04	2.3E+06
BISO	water	air	–	6.3E+03	1.4E+06
BISO	brine-2	argon	+	9.2E+01	2.1E+04
TRISO	brine-2	argon	+	3.1E+01	7.0E+03
BISO	water	argon	+	2.2E+03	4.9E+05
TRISO*	brine-2	argon	+	5	–
BISO*	brine-2	argon	+	21	–

* – lifetimes were calculated from data obtained in experiments with intact coated particles

D.2. Graphite treatment

In order to study the release of radionuclides during graphite treatment at high temperature, experiments in inert and water steam atmosphere were carried out. The investigations were performed with graphite samples from the Merlin reactor and AVR.

D.2.1. Treatment in argon atmosphere

D.2.1.1. Tritium release

The amount of tritium released from Merlin and AVR graphite at different temperatures in inert atmosphere is shown in Figure 31.

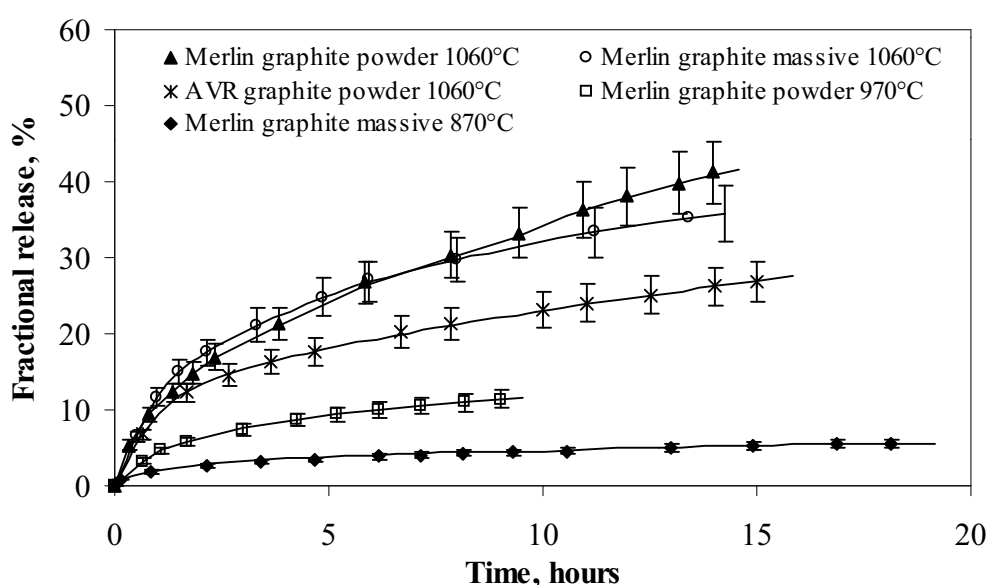


Figure 31. Tritium release in argon atmosphere

In all experiments, two different tritium release stages were observed. At the beginning, tritium was released faster, which corresponds to the region of the release curves with high ascending slope. This can indicate that there was desorption of ^3H from active sites located on the surface. In the second stage, the release became moderated with time and was of a linear character.

Two samples of Merlin graphite were investigated at a temperature of 1060°C: powder and massive sample. It can be seen that the amount of released ^3H was almost the same for both samples. Therefore it can be considered that tritium release from the graphite sample was not limited by diffusion in pores. The increase of ^3H release from the powder sample in comparison with massive sample after 9 hours can be explained by oxygen ingress into the system causing oxidation of the graphite sample and increase of released tritium.

The maximum value of released tritium was obtained from Merlin graphite powder. It amounted to 43% after 15 hours. Reduction of the temperature caused a decrease in ^3H release. At 970°C the amount of tritium released was about 10 % after a 9-hour treatment.

For AVR graphite the amount of tritium evolved at the same temperature was approximately 27 %. This difference can be explained by different operational conditions for these two

materials. The AVR is a pebble-bed gas-cooled reactor and the average gas-outlet temperature was about 950°C [27, 76], whereas in Merlin reactor, light water is the moderator and coolant. The operational temperature of thermal columns is ambient in this case [77].

It is reported in a number of publications that the mobility of hydrogen molecules in undamaged graphite is rather slow [41, 78, 79]. In AVR the operational temperatures are rather high and some of the defects caused by neutron irradiation can be annealed. The other reason may be related to the fact that under the high temperature conditions of AVR tritium diffuses inside graphite grains [15, 41].

D.2.1.2. ^{14}C release

^{14}C release is shown in Figure 32. The maximum value was obtained for Merlin graphite at 1050°C and amounted to 20 %. The release of radiocarbon is slightly higher in the initial period of time. This possibly represents the elimination of ^{14}C in the composition of oxygen complexes from the graphite surface, which can be easily eliminated by heating. The other possibility may be an interaction of carbon with adsorbed oxygen. A drastic increase of ^{14}C release in this experiment after 9 hours of heating was related to oxygen ingress, as it was mentioned above. In can be seen that oxidation of the graphite increased the radiocarbon release twofold although the mass loss of the sample was not significant (1.36 %).

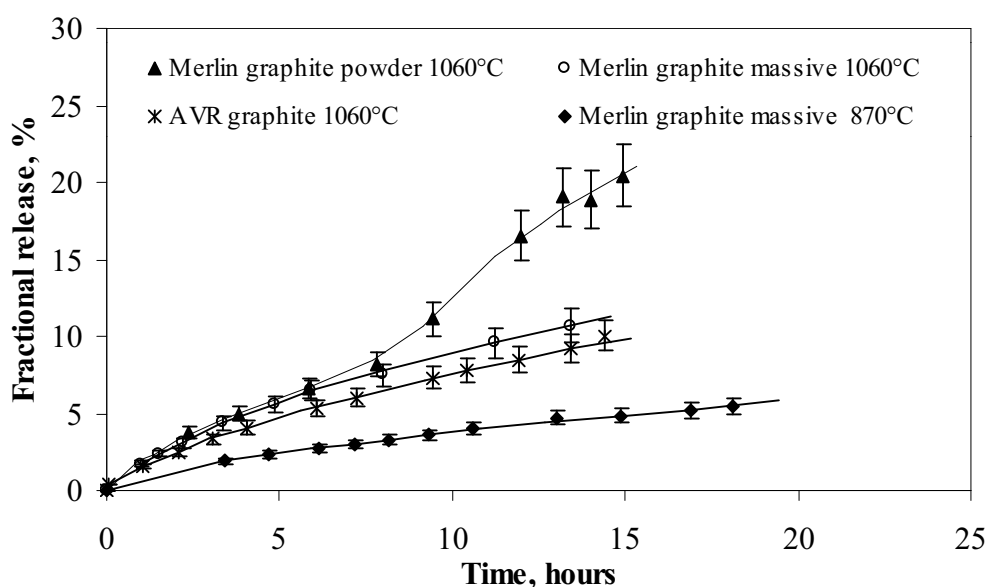


Figure 32. ^{14}C release from AVR and Merlin graphite in argon

The total fractional release of ^{14}C is less than the fractional release of tritium because the location of these radionuclides in the graphite matrix is different. This will be discussed later in Chapter D.2.3.

It should be noted that during thermal treatment in argon atmosphere a small concentrations of CO and CO₂ were observed in carrier gas outlet. However, the sample mass loss was negligible and amounted to 0.16–1.36%.

D.2.2. Oxidation with water steam

Experiments in water vapour were carried out in order to study the influence of oxidation on the release of tritium and ^{14}C . The saturated water vapour pressure was 2.3 kPa and 7.4 kPa. Additionally, one experiment with Merlin graphite was performed in water steam at a vapour pressure 70 kPa with a successive increase of the treatment temperature.

D.2.2.1. Tritium release

^3H release during graphite oxidation with stepwise increased temperature is shown in Figure 33. Tritium started to be released at 400°C in small amounts (1.3 % after 5 hours). As can be seen from the release curve slope, the release rate increased with temperature. The whole tritium inventory was removed from the graphite sample after 20 hours of thermal treatment. The total mass loss of the sample amounted to approximately 50 %.

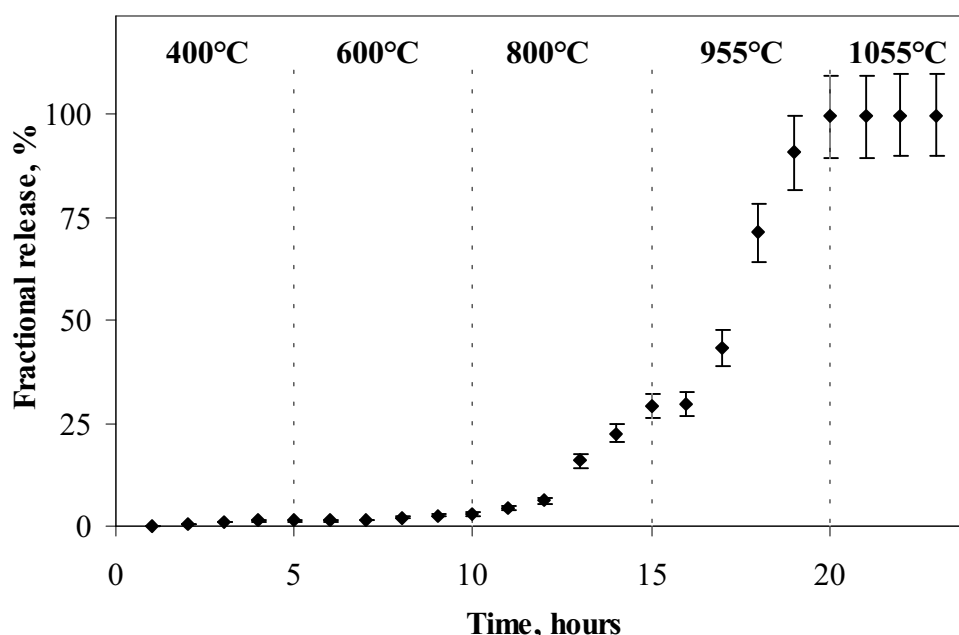


Figure 33. Tritium release with stepwise temperature increase by oxidation in water steam at vapour pressure 70 kPa

^3H release from Merlin graphite powder at temperatures of 960°C and 1060°C during oxidation with water steam at a vapour pressure 7.4 kPa is presented in Figure 34 (a). The graphite oxidation caused an increase of the total tritium release in comparison with the experiment in argon atmosphere (see Chapter D.2.1 Figure 32).

At 960°C experiments were performed at two different flow rates of carrier gas. The influence of flow rate on ^3H release was observed: the increase of argon flux from 80 mL/min to 660 mL/min gives a more than twofold increase of tritium release from 30 % to 65 %. The sample mass loss in these experiments was 3.2 and 4 %, respectively, (Figure 36 b), which is higher in comparison with graphite treatment in argon atmosphere.

At 1060°C, about 90 % of the total tritium inventory was removed from Merlin graphite after 8 hours accompanied by a sample mass loss of 32 % (the mass loss of the samples with time is shown in Figure 36 b in Chapter D.2.2.2).

The results of graphite treatment at lower water vapour pressure (2.3 kPa) are shown in Figure 34 b. One can see that the same amount of tritium was released from Merlin graphite at the temperature of 1060°C after 8 hours as in the experiment with water vapour pressure 7.4 kPa (Figure 34 (b)). The corresponding sample mass loss was 22% (Figure 37 b). For AVR graphite, the fraction of released tritium is less than from Merlin graphite as well as in the experiments under inert atmosphere.

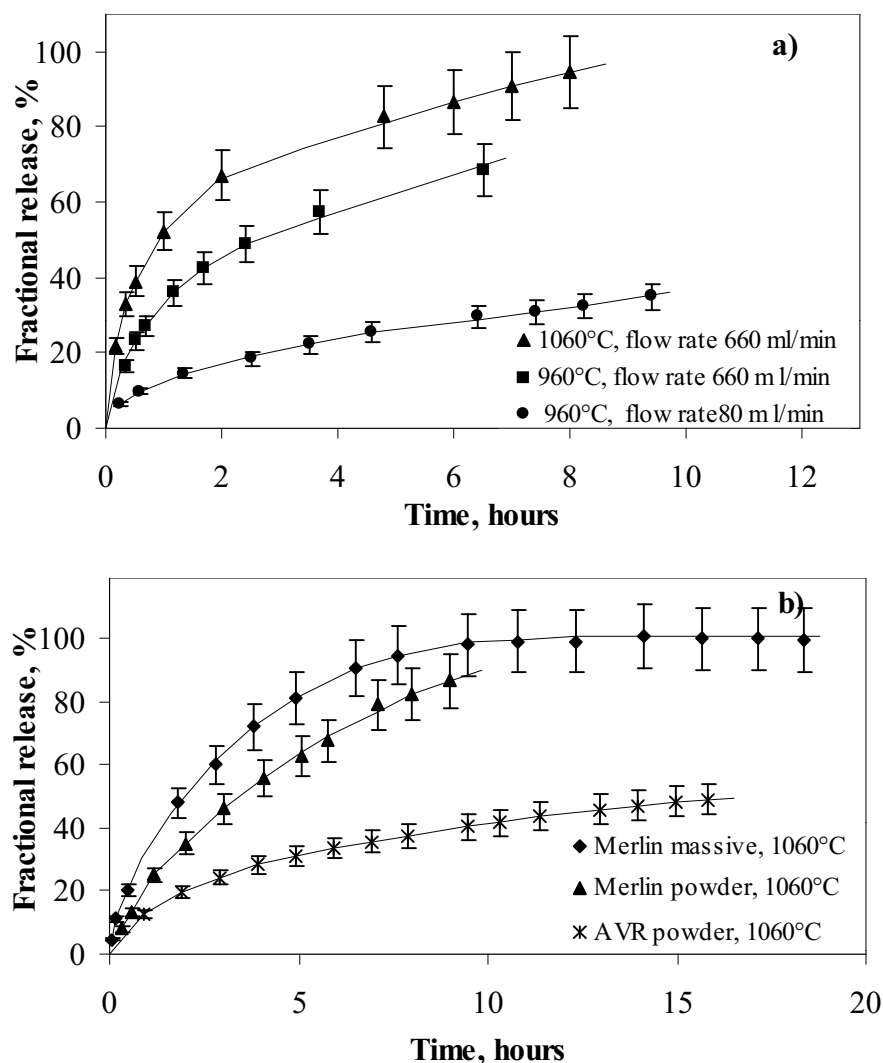


Figure 34. a – Tritium release from Merlin graphite powder during oxidation at saturated water vapour pressure 7.4 kPa; b – Tritium release from Merlin and AVR graphite at 1060°C and saturated water vapour pressure 2.3 kPa

D.2.2.2. ^{14}C release

The oxidation process influences the ^{14}C release in a manner similar to the case of tritium. As was shown in the experiments with stepwise increase of oxidation temperature, ^{14}C release started at 600°C (Figure 35). The quantity of evolved ^{14}C was very small due to negligible reaction rate of graphite and water steam at this temperature. At 800°C a fast increase of radiocarbon release (about 18 % after 1 hour) was observed at the beginning. After that ^{14}C release was rather slow. It can be related to graphite surface oxidation by adsorbed oxygen.

Probably, the ingress of air occurred during cooling of the system between experiments, when argon flushing was stopped. Oxygen from the air could be adsorbed chemically on the graphite surface and removed through CO and CO₂ formation after the next heating stage.

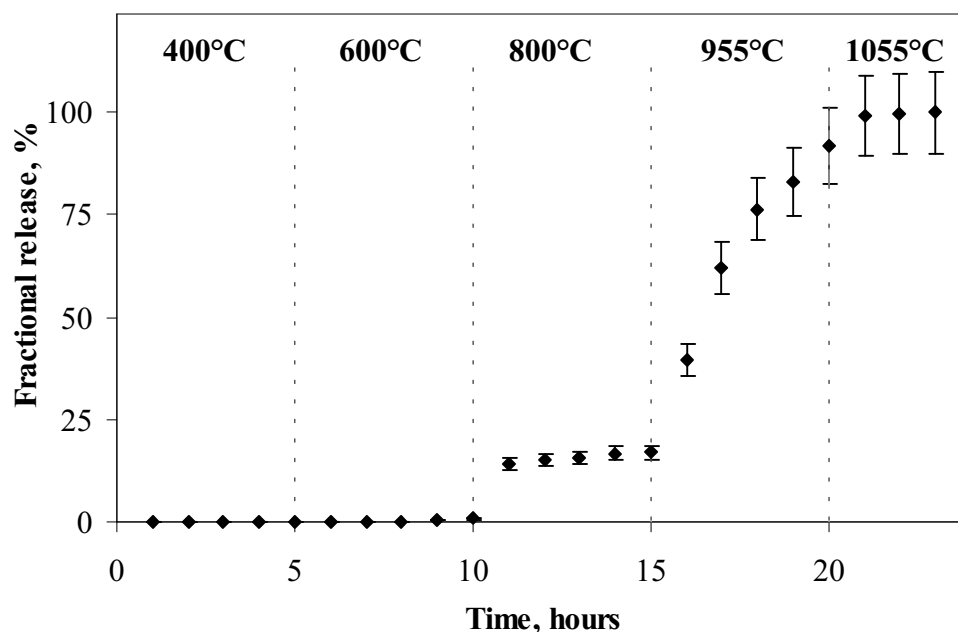


Figure 35. ¹⁴C release with step-by-step temperature increase by oxidation in water steam at vapour pressure 70 kPa

Based on these results, further experiments were performed at temperatures above 900°C because significant ¹⁴C release by treatment in water steam was observed under these conditions. ¹⁴C release from Merlin and AVR graphite is presented in Figure 36 (a, b).

It can be seen from Figure 36 a and Figure 37 a that elimination of radiocarbon increases in comparison with treatment in argon (Figure 32). This is connected with oxidation of graphite matrix release leading to release of ¹⁴C located in the nodes of graphite lattice.

In order to compare the release of ¹²C and ¹⁴C simultaneously, the mass loss of the sample with time was determined (Figure 36 b and Figure 37 b). One can see that the loss of 65 % inventory of ¹⁴C after 14 hours at 1060°C corresponds to the mass loss of ~ 42 %. As a result, we have a ratio of about 1.5 for released ¹⁴C to oxidised ¹²C.

At a temperature of 960°C an experiment was performed with two different flow rates. As in the case of tritium, with increasing flow rate the amount of ¹⁴C released also increased from 11 % to 24 % after 7 hours. The mass loss of graphite sample amounted to 2.5 % and to 4 %, respectively. This gives the ratio of released isotope fractions as 4.4 and 6, correspondingly. Comparing these results with treatment at a higher temperature (1060°C) after 7 hours, it can be concluded that the graphite oxidation at a lower temperature is more effective in order to eliminate ¹⁴C without significant burn-off of the total graphite mass.

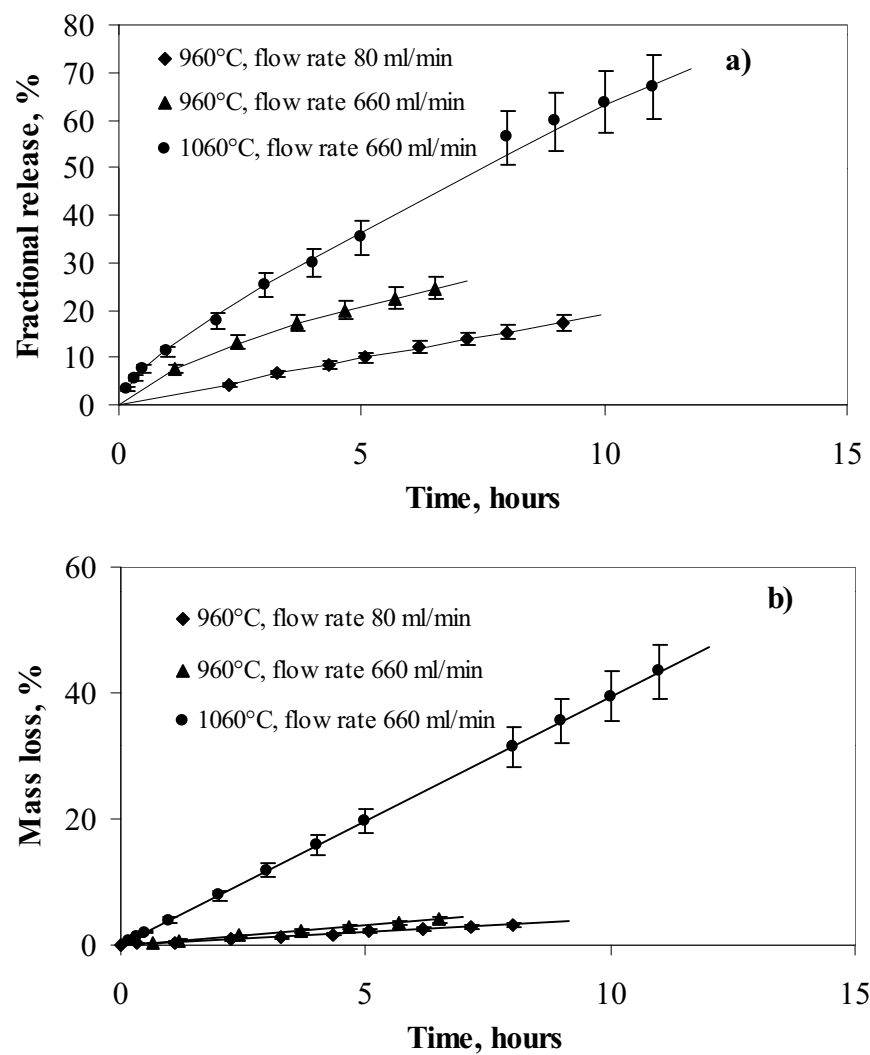


Figure 36. ^{14}C release (a) and mass loss (b) during Merlin graphite oxidation with water steam (water vapour pressure 7.4 kPa)

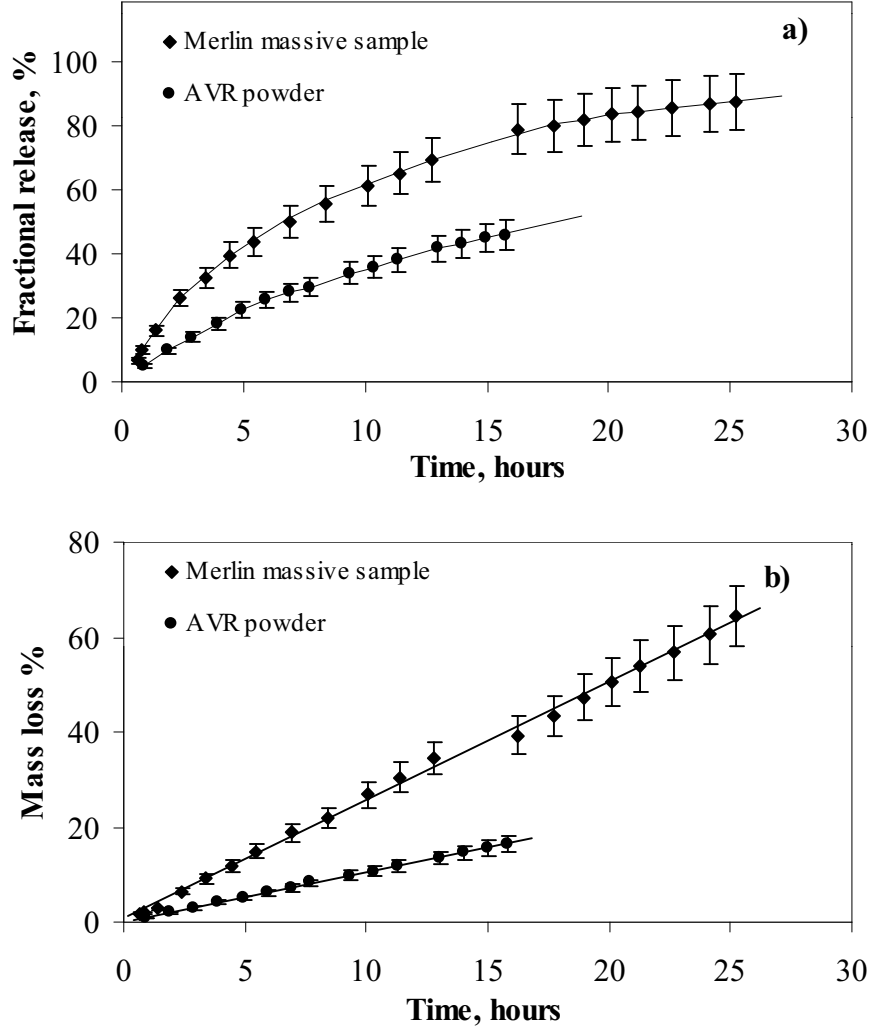


Figure 37. ^{14}C release (a) and mass loss (b) during Merlin and AVR graphite oxidation with water steam at 1060°C (water vapor pressure 2.3 kPa)

D.2.3. Release rates

The kinetics of radionuclide i release can be described in the form of release rates R_i . The release rates of radionuclides were determined by the following equation:

$$R_i = \frac{x_i(t_j) - x_i(t_{j-1})}{m(t_{j-1}) \cdot (t_j - t_{j-1})} \quad \text{Eq. (58)}$$

$x_i(t_j)$ – the released amount of component i at the time t_j , (mol)

t_j – time at the moment j , (hours)

m_{t_j} – mass of the graphite sample at the time t_j , (g)

The release rate of radioactive components such as ^3H and ^{14}C is certainly much lower than the oxidation rate of ^{12}C because their content in graphite is very small (10^{-11} mol/g of ^3H and 10^{-10} mol/g of ^{14}C in Merlin graphite). However, the fractional release of tritium and ^{14}C is

higher than the fraction release of ^{12}C . For example, the following graph (Figure 38) shows the release rates and released amount of ^{12}C , ^{14}C and ^3H from Merlin graphite (massive sample) during oxidation in water steam at 1060°C and 2.3 kPa water vapour pressure.

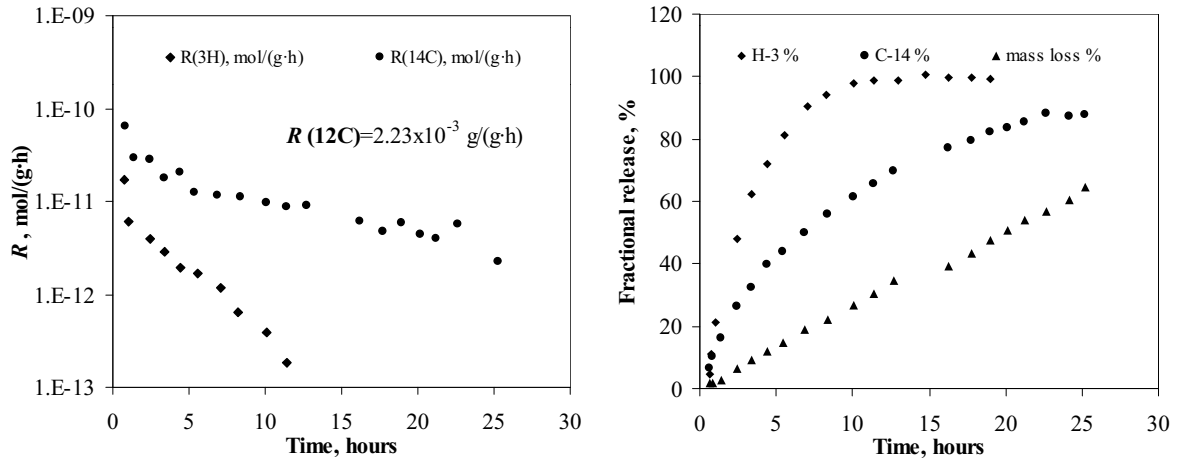


Figure 38. Release rates and released amounts of ^{14}C , ^{12}C and ^3H from Merlin graphite oxidised in water steam at 1060°C and water vapour pressure 2.3 kPa.

The release rate of radioactive elements can be compared directly with those of the other elements by normalising with the factor f_i , which is the molar fraction of element i in the graphite body. The normalised release rates of components were determined as:

$$NR_i = \frac{R_i}{f_i} \quad \text{Eq. (59)}$$

$$f_i = \frac{v_i}{v_{^{12}\text{C}}} \quad \text{Eq. (60)}$$

where v_i – amount of element i , (mol).

The ratio of normalised release rate of radionuclide i to normalised release rate of matrix component (^{12}C) can be denoted as:

$$K_i = \frac{NR_i}{NR_{^{12}\text{C}}} \quad \text{Eq. (61)}$$

D.2.3.1. Release rates under inert atmosphere

Tritium normalised release rates

The ratios of tritium normalised release rates under inert atmosphere are presented in Figure 39. It can be seen that at all temperatures in inert atmosphere tritium evolved faster than ^{12}C from the graphite matrix. The release rate ratio decreased with time and later became constant. The high rate ratio at the beginning can be related to desorption of radionuclides from the edge planes of graphite and imperfections of graphite structure. The ratio of release rate of ^3H to ^{12}C increases with increasing treatment temperature from 10 at 870°C to ~50 at 1060°C.

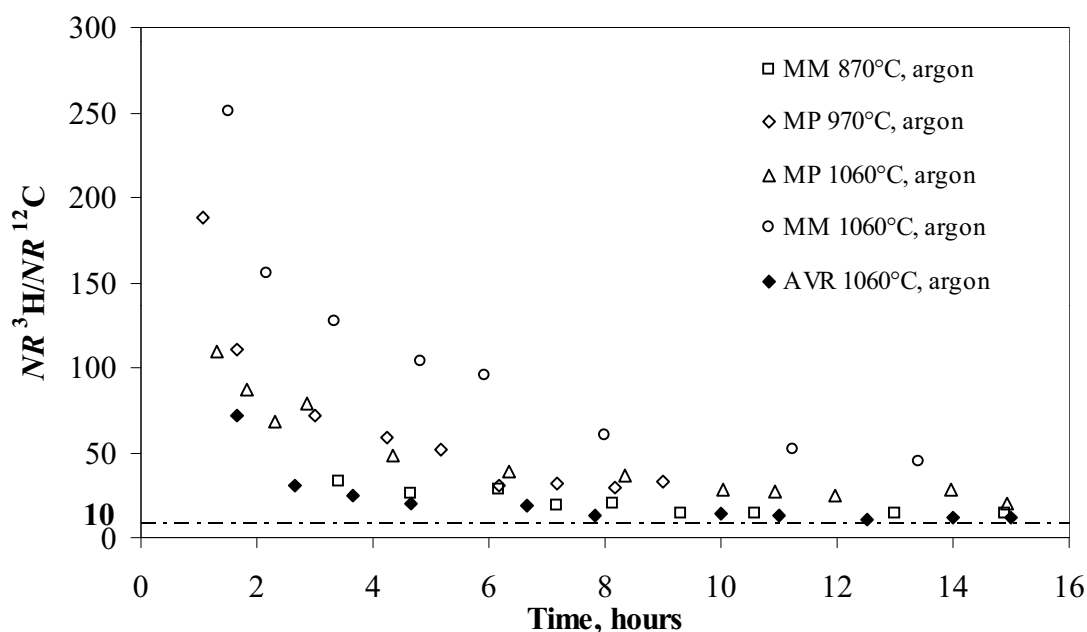


Figure 39. Ratio of normalised release rate of ^3H to normalised release rate of ^{12}C in inert atmosphere

As has been established [80], hydrogen atoms are trapped at the edges of the graphene sheets and between the graphene layers near the particle surface. Two kinds of trapping sites exist for hydrogen retention [81–83]. One is an interstitial cluster loop edge or solitary dangling bond located in a crystallite with adsorption enthalpy of 4.4 eV. The other is a carbon dangling bond located at the edge surface of a crystallite with an enthalpy of 2.3 eV [83] (Figure 40). In the case of neutron- or ion-irradiated graphite, the Trap 1 sites dominate hydrogen retention and Trap 2 are important in the case of unirradiated graphite.

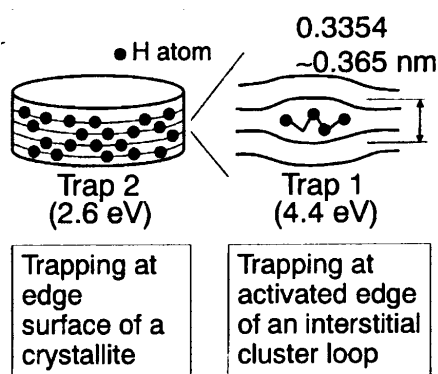


Figure 40. Model of hydrogen trapping sites in a graphite material

Desorption of hydrogen starts at $\sim 300^\circ\text{C}$ and has two maxima around 450°C and 780°C [84]. The first peak is considered to be due to hydrogen desorbed from defective sites between graphite sheets, and the second one originates from the covalent bonding sites.

The release of tritium from graphite grains is controlled by the diffusion process. Tritium atoms desorb from the trapping sites. Then their association reaction takes place at the open

pores as well as on the inner and outer surface of polycrystalline particles, and tritium molecules can diffuse away through open pores to free space.

The mechanism of tritium diffusion in graphite is described in details in the literature. Numerous studies have been performed on hydrogen diffusion and retention in graphite [41–44, 81, 82, 84].

Most commercial graphites are not single crystalline materials, but consist of aggregates of polycrystalline particles. The microstructural model is presented in Figure 41. It is assumed [43] that the tritium atoms captured by carbon atoms diffuse in a crystalline grain along the a - and c -axis. In addition, tritium atoms can also diffuse along the grain boundaries [85]. Three distinct diffusion channels are indicated in Figure 41 by arrows: 1 – along the a -axis in a grain, 2 – along the c -axis in a grain and 3 – along the grain boundary. Diffusion through path 2 does not appear to be plausible because of the long-distance carbon network and hence considerable large activation energy.

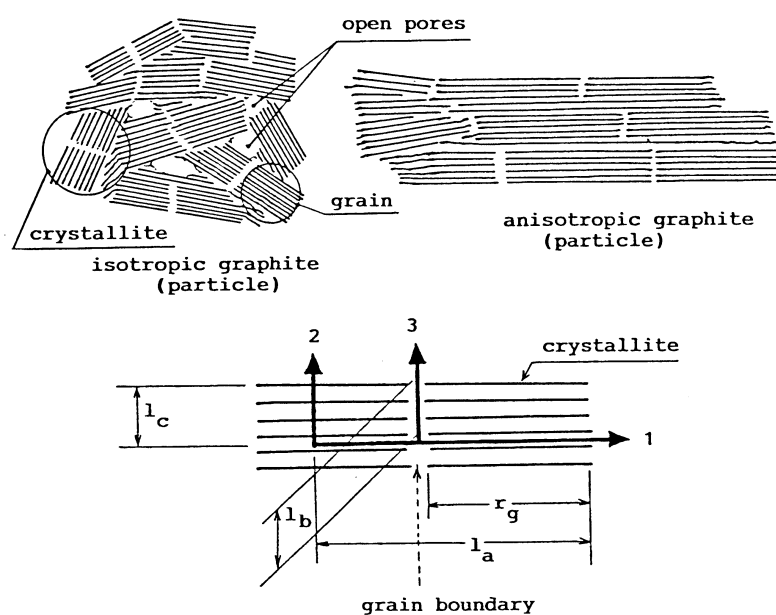


Figure 41. Microstructural models of isotropic and anisotropic graphite

Diffusion coefficients of tritium in graphite

Diffusion coefficients of tritium in graphite can be determined from tritium release curves during isothermal heating of contaminated graphite samples. The fractional release of tritium from graphite $F(t)$ can be plotted as a function of the square root of the heating time, $t(s)$. As can be seen from Figure 42, tritium release fits well with this function. The diffusion coefficient, D ($\text{cm}^2/\text{s}^{-1}$), was calculated from the slope of the linear portion of the curve using the following relation, which was derived from Fick's law [86]:

$$F(t) = 4\sqrt{\frac{Dt}{\pi}} \cdot \frac{1}{R} \quad \text{Eq. (62)}$$

for $F(t) \leq 0.3$

R – the recoil range of tritium from ${}^6\text{Li}(n,\alpha){}^3\text{H}$ reaction in graphite. The recoil range for graphite was taken from the literature and amounted to $32\text{ }\mu\text{m}$ [86, 87]. Results of the calculations are presented in Table 22.

Table 22. Diffusion coefficients of tritium in Merlin and AVR graphite

Type of graphite	Temperature, °C	Diffusion coefficient D , $\text{cm}^2/\text{s}^{-1}$
Merlin	870	5.70E-14
Merlin	970	7.40E-13
Merlin	1060	6.19E-12
AVR	1060	1.70E-12

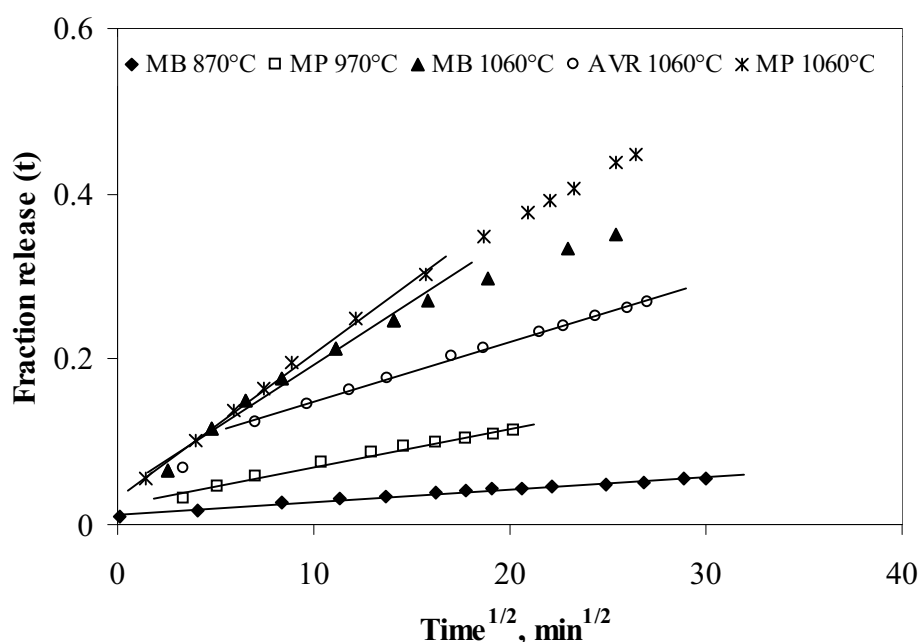


Figure 42. Tritium release vs. square root of the treatment time

Figure 43 shows an Arrhenius plot of logarithmic diffusion coefficients for Merlin graphite vs. $1/T$ (°K). The activation energy was calculated from the slope as 323 kJ/mol and the pre-exponential factor as $10.7\text{ cm}^2/\text{s}$.

The pre-exponential factor and activation energy are different for different types of graphite due to classification of the diffusion paths [43]. The diffusion of tritium in highly oriented graphite or highly anisotropic graphite will be slower than in isotropic graphite, because the tritium atoms hardly penetrate the layer plane. As was shown by Saeiki [44] the activation energy of the diffusion process in graphite samples with a high value of the anisotropy factor was in the range of 250–260 kJ/mol, whereas the activation energy for isotropic pyrographite amounted to 105 kJ/mol. In the case of laminar graphite [87], with a quite large parameter l_a the activation energy is 412 kJ/mol for diffusion along grain boundaries. The values of pre-exponential factor and activation energy obtained for Merlin graphite in the present work are typical of nuclear graphite with a high anisotropy factor.

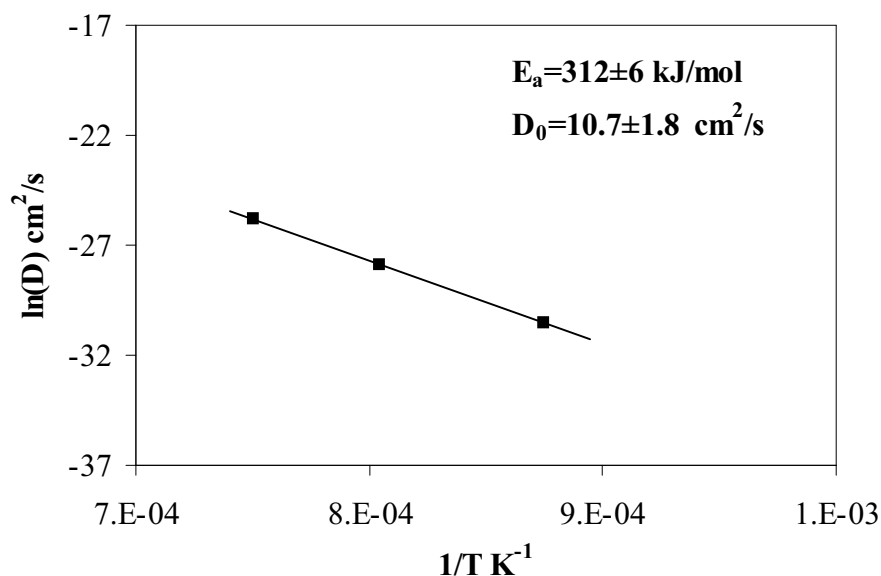


Figure 43. Arrhenius plot for tritium diffusion in Merlin graphite

^{14}C normalised release rates

The ratio of the carbon isotope release rate ($K_{^{14}\text{C}/^{12}\text{C}}$) was lower than in the case with tritium (Chapter D.2.3.1, Figure 39). The highest K value was observed for Merlin graphite by treatment at 870°C in argon. As can be seen from Figure 44, the K value was close for Merlin graphite treatment at 1060°C and 870°C. A higher release rate of ^{14}C in comparison to ^{12}C means that this radionuclide is not distributed homogeneously in the graphite grains otherwise it would be released at the same rate as ^{12}C . Therefore it can be supposed that the graphite surface near grain boundaries is enriched with ^{14}C .

Information about ^{14}C localisation in graphite was not found in the literature. It is known that ^{14}C is an activation product originating mainly from nitrogen impurities in graphite matrix or from nitrogen adsorbed on the surface from the gas cooler [30]. The contribution of ^{13}C and ^{17}O are of less importance.

One possibility for the ^{14}C position in a graphite crystal is adsorption on the edge planes of the graphite surface. Oxygen functional groups on carbon surfaces decompose to carbon oxides upon heating in an inert atmosphere [88]. The complexes yielding CO_2 were shown to decompose typically over a range of temperatures starting at 200°C and exhibiting desorption maxima at 300°C and 600°C [89]. Carboxylic acids have been proposed to be predominantly responsible for the low-temperature peak. The high-temperature CO_2 evolution has been attributed to carboxylic anhydrides. Similarly, the CO -yielding groups have a CO evolution maximum at 900 and 1100 K. The total desorbed quantity of CO and CO_2 amounted to 19 $\mu\text{mol/g}$ for graphitised carbon fibres with a specific surface area of 6 m^2/g . This corresponds to 0.023 % of mass loss. In the present experiments, mass loss varied in the range from 0.16 to 1.6 %. Thus this carbon cannot be related to the desorption of functional groups alone but also to slow oxidation caused by the presence of oxygen traces in the inert carrier gas. Moreover, desorption would take place in the initial period of time, whereas constant release of ^{14}C from the sample was observed throughout the heating procedure.

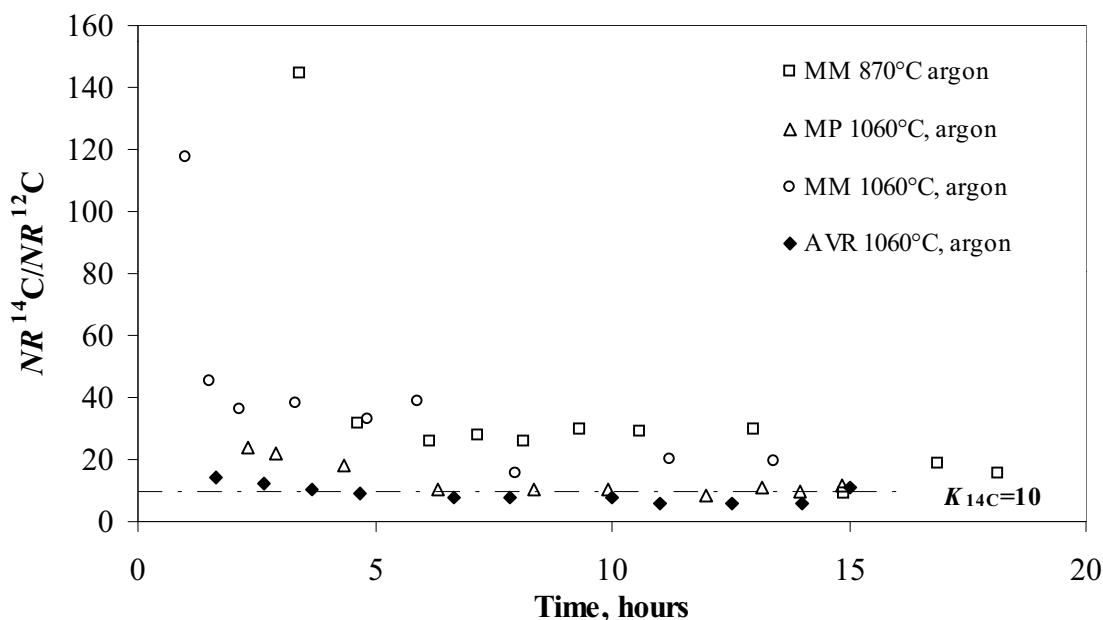


Figure 44. Ratio of normalised release rate of ^{14}C to normalised release rate of ^{12}C in inert atmosphere

The other possibility of radiocarbon arrangement in graphite is intercalation between graphite layers or embedding in graphite lattice under neutron irradiation [90]. ^{13}C also can be a source of ^{14}C uniformly distributed in the graphite matrix. Being in the composition of graphite lattice, ^{14}C can be removed only by oxidation because carbon diffusion in the basal plane is significant only above 2200°C [34].

A carbon atom displacement caused by neutron or ion irradiation results in crystallite dimensional changes [20]. Two types of damage centres are known – vacancies and interstitials. Interstitials cause crystallite growth perpendicular to the layer planes (c-axis direction) and coalescence of vacancies causes shrinkage parallel to the layer plane (a-axis direction). During thermal treatment annealing of the lattice defects occurs. Interstitials start to migrate to the edge surface or to reintegrate with vacancies [20, 91, 92]. If ^{14}C is in the composition of interstitials it can be supposed that during heating in inert atmosphere diffusion of ^{14}C from graphite can be attributed to diffusion of interstitials from the interlayer space to the edges of graphite planes with their subsequent desorption. But, as was already mentioned above, the presence of a constant concentration of CO and CO₂ of a few ppm in the carrier gas flow supposes the presence of oxygen in the system. Therefore the conditions were not absolutely “oxygen-free” and release of ^{14}C caused by oxidation cannot be excluded.

D.2.3.2. Release rates under oxidising conditions

Normalised release rates were calculated for the oxidation of Merlin graphite with water steam (water vapour pressure 7.4 kPa and 2.3 kPa) at temperatures of 1060°C and 960°C. The release rates ratios of ^3H and ^{14}C to ^{12}C are presented in Figure 45 and Figure 46.

It can be seen from Figure 45 that at 960°C velocity of the carrier gas affects the ratio of the release rate of tritium and ^{12}C . At lower argon velocity (80 mL/min) $K_{3\text{H}}$ was about 10. At higher argon flow velocity (660 mL/min) the ratio of release rates of ^3H to ^{12}C increased up to 23.

In the case of ^{14}C , it can be seen from Figure 46 that the release rate ratio of ^{14}C to ^{12}C did not depend on the gas velocity and amounted to ~ 7 .

At 960°C , the reaction with water steam is closer to the regime of the first reaction zone (see B.1.2) [4]. The reaction rate in this temperature zone is low and is determined by the intrinsic reactivity of the graphite. Different parts of the graphite structure may react at different rates: edge atoms being more reactive than basal plane atoms.

The reaction rate of bulk graphite with water steam increased with temperature up to 1060°C . For both radionuclides the ratio of release rates to ^{12}C release was decreased in comparison with 960°C . After the initial period of time, the release rate of ^{14}C approached almost the same value as the rate of matrix oxidation. The influence of water vapour pressure on the release rate of radionuclides and matrix oxidation can be observed by comparing the results of graphite treatment at 2.3 kPa and 7.4 kPa saturated water vapour pressure at the temperature of 1060°C . At 7.4 kPa normalised release rates were higher, but the ratio of the normalised release rate of tritium to graphite matrix oxidation rate was lower. For ^{14}C this value did not change in comparison with experiments at 2.3 kPa saturated water vapour pressure.

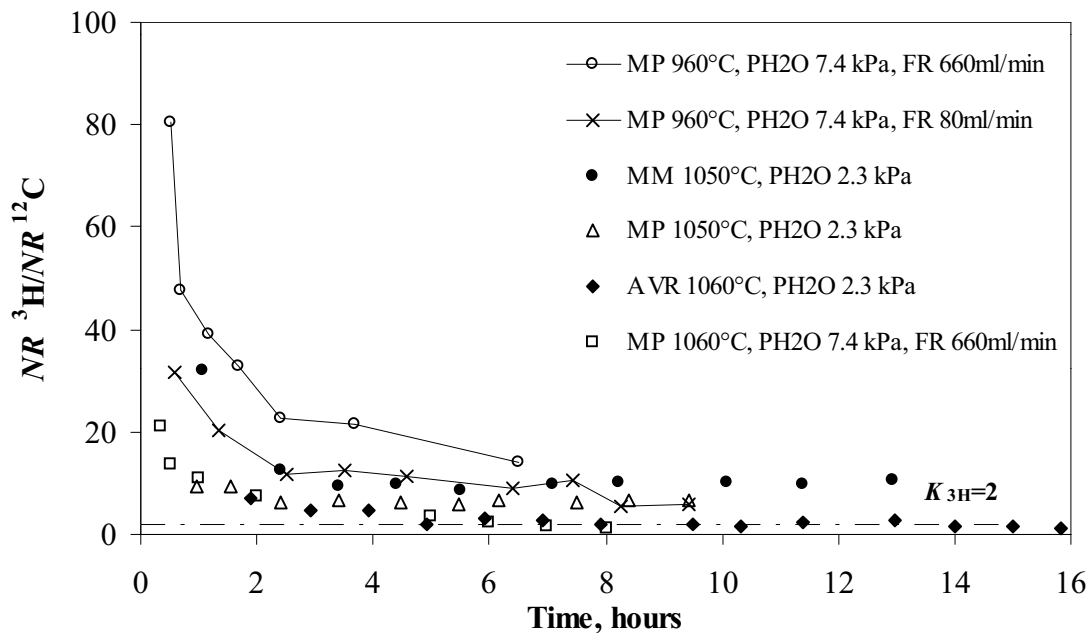


Figure 45. Ratio of normalised release rates of ^3H to ^{12}C in oxidising atmosphere

The results obtained for AVR graphite after treatment in water steam differ from those obtained for Merlin graphite. It is typical of AVR graphite that ^{14}C and ^3H were released with the same rate during oxidation. This can be explained from the fact that tritium in AVR reflector graphite diffuse inside the graphite crystal at high temperatures of reactor operation and can be blocked by carbon atoms displaced from the lattice under neutron irradiation into interplanar space. Apparently, during oxidation of graphite release of these trapped tritium atoms occurs.

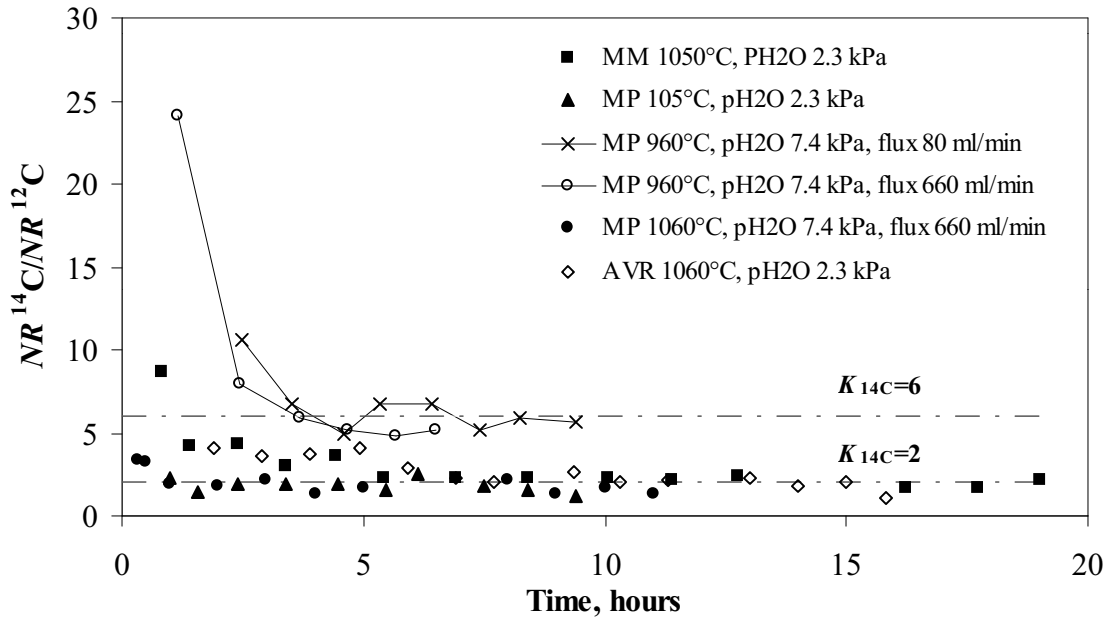


Figure 46. Ratio of normalised release rate of ^{14}C to normalised release rate of ^{12}C in oxidising atmosphere

D.2.3.3. Comparison of treatment regimes

The main parameter determining the efficiency of contaminated graphite treatment without complete combustion is the ratio of fractional release of radionuclides to mass loss of graphite.

According to the difference in the release rate ratios of radionuclides depending on treatment conditions, the results on ^{14}C and tritium release are summarised and compared in Figure 47 and Figure 48.

From Figure 47 region I, it can be assumed that ^{14}C release was not caused by diffusion of interstitials from interplanar space because in this case the temperature dependence of ^{14}C release would be clearly seen. Apparently, the graphite grain boundaries are enriched with ^{14}C and its concentration decreases with depth inside the graphite grains as can be observed by oxidation of graphite at low temperatures or by small concentrations of oxidant.

A suitable method for ^{14}C release from contaminated graphite is slow selective oxidation of graphite edge planes in order to remove the “contaminated” zone.

In contrast to ^{14}C , tritium fraction release curves in argon atmosphere (region I, Figure 48) show a significant difference in the amount of ^3H released at different temperatures with the same mass loss. The experiments in water steam at high temperatures lie in region II below the dashed line 20:1. In this region tritium fractional release is still rather high in comparison to sample mass loss (line 1:1).

It can be considered for tritium that treatment at high temperatures in inert atmosphere is sufficient to release this radionuclide from graphite.

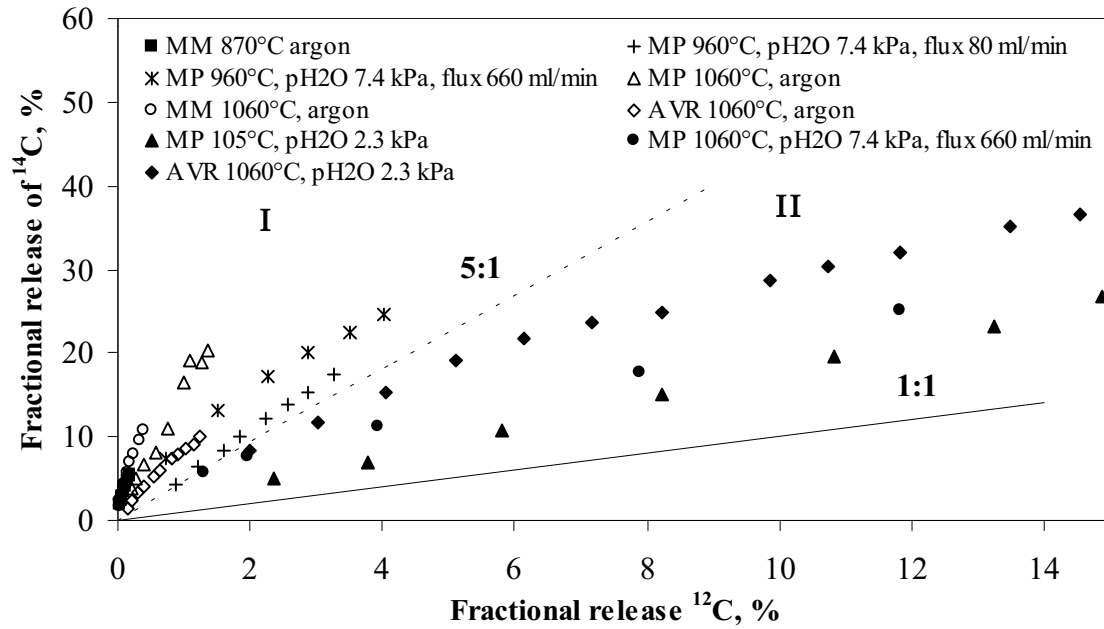


Figure 47. ^{14}C release vs. fractional release of ^{12}C during treatment under different conditions (MM – Merlin graphite massive sample, MP – Merlin graphite powder)

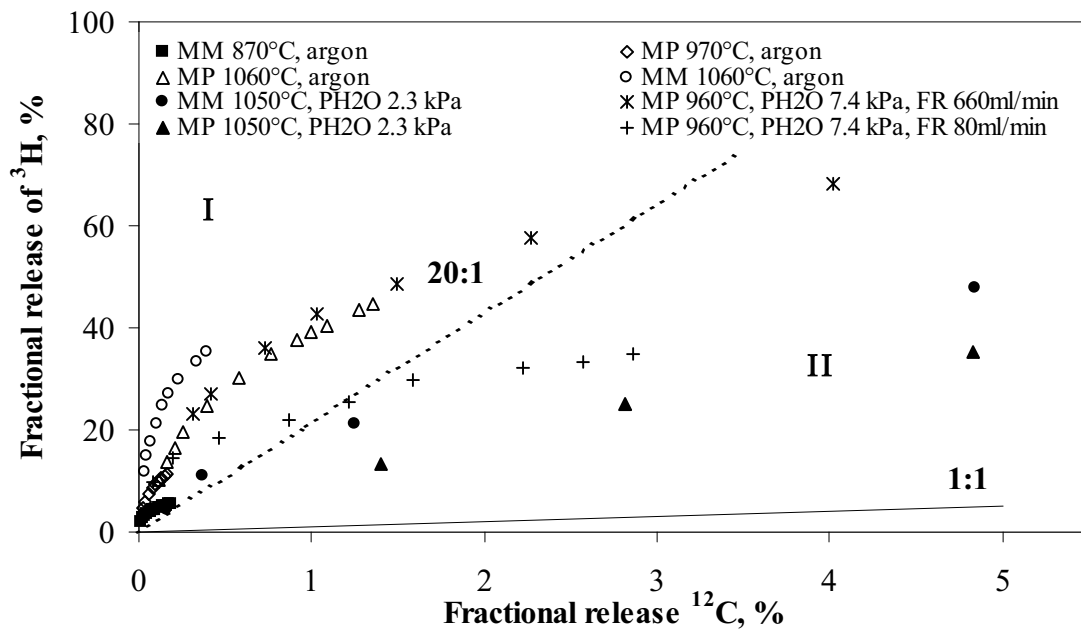


Figure 48. ^3H release vs. fractional release of ^{12}C during treatment under different conditions (MM – Merlin graphite massive sample, MP – Merlin graphite powder, FR – flow rate)

D.2.4. Migration of other radionuclides during graphite thermal treatment

The measured γ -activity of Merlin and AVR graphite correlates with previously reported data [93, 94] (Table 47, Table 48).

In the case of Merlin graphite, the inventory of the main contaminants such as ^{60}Co , $^{154,155}\text{Eu}$ and ^{133}Ba was not very high (Table 48 in appendix).

Analysis of residue remaining in the reaction boat after complete combustion of graphite sample revealed that virtually all radionuclides stayed in the ceramic boat and could be recovered by rinsing in concentrated HCl (Table 23).

Table 23. Results of γ - and total γ , β -activity measurements of Merlin graphite samples

Radionuclide	Average activity Bq/g	960°C	1060°C	1060°C
		$p_{\text{H}_2\text{O}}$ 7.4kPa Bq/g	$p_{\text{H}_2\text{O}}$ 7.4kPa Bq/g	argon Bq/g
Eu-152	640	689	742.6	624
Cs-137	0.18	—	—	—
Co-60	536	553	581	389
Total β - γ activity	1355	1258	1312	1419

Average activity was determined in independent experiments by complete combustion of graphite samples in oxygen.

In AVR graphite, ^{133}Ba , $^{154, 155}\text{Eu}$, $^{134, 137}\text{Cs}$ and ^{60}Co are present in larger amounts than in Merlin graphite. After experiments in argon atmosphere for 15 hours at 1060°C, analysis of the reactor tube showed no radionuclide contamination. After post-experimental graphite burning, ^{133}Ba , $^{154, 155}\text{Eu}$ and ^{60}Co were found almost completely in the rinse from the ceramic boat. As was expected from literature data [39], these radionuclides were not volatilised at this temperature and remained in the combustion chamber.

The radionuclide inventory measured in the rinse and boat is listed in Table 24. The total content of every radionuclide was calculated as an average from the analysis of AVR graphite samples (Table 47 in appendix). Therefore scattering between the total amount of radionuclide and its recovery can be attributed to inhomogeneity of radionuclide distribution in graphite.

The behaviour of Cs was less evident. About 30% of the total content was found in the reaction boat. The rest of the Cs was considered to diffuse from the graphite and later become volatilised because of the high experimental temperature of 1060°C. It is known that at this temperature Cs can be transported to the gas phase due to volatilisation [26, 39]. However, Cs was not detected in the reaction tube rinse and in the washing bottles.

During water steam oxidation of AVR graphite (water vapour 31 kPa) at 1060°C, no contamination of the reaction tube was observed. The results of γ -analysis of the residue and reaction boat are presented in Table 25. It can be seen that the main radionuclide inventory was detected in the reaction boat.

This can be effectively used for cleaning graphite of these contaminants.

Table 24. Radionuclide distribution after treatment of AVR graphite in argon atmosphere

Radionuclide	Total content	Rinse from reaction boat	Reaction boat
	Activity, Bq		
Ba-133	304±46	233±35	9±1
Eu-154	124±19	100±15	2
Eu-155	33±5	30±5	–
Cs-134	36±5	–	11±2
Cs-137	607±91	5.9±1	200±30
Co-60	2604±390	2500±375	102±15

Table 25. Radionuclide distribution after treatment of AVR graphite in water steam (water vapour pressure 31 kPa)

Radionuclide	Total content	Rinse from reaction boat	Reaction boat
	Activity, Bq		
Ba-133	103±16	18±3	54±8
Eu-154	42±6	9±1	15±2
Eu-155	12±2	5±1	–
Cs-134	12±2	–	10±1
Cs-137	207±31	–	165±25
Co-60	1249±187	15±2	1450±218

E. Summary and outlook

The proposed solution for HTR spent fuel management in Germany is direct disposal in deep geological formations. Three types of rocks are considered as host units – salt domes, clay and granite. In addition to the geological and engineered barriers the long-term safety of the repository depends on the integrity of the fuel element consisting of coated particles embedded into a graphite matrix. As an accident scenario the water ingress into a repository and its interaction with the protective barriers of graphite and the pyrocarbon coatings must be taken into account. In this connection, the behaviour of graphite and pyrocarbon in repository relevant conditions is important.

In the present work, the corrosion of the graphite matrix of spherical fuel element and pyrocarbon coatings from unirradiated fuel particles in different aqueous phases was investigated. As aqueous media deionised water, MgCl_2 -rich (brine-2) and NaCl -rich (brine-3) solutions were used. The experiments were performed under argon, oxygen and air atmosphere at 90°C . Also the influence of γ -irradiation on corrosion process in anoxic conditions was investigated. Corrosion rates were calculated from CO and CO_2 production.

In leaching experiments performed in MgCl_2 -rich solution and water under inert atmosphere only negligible amounts of CO_2 were found in the gas phase after two years. The analysis of the gas phase composition revealed the absence of hydrogen, which indicates that corrosion is not caused by the interaction of graphite and water. Therefore it was considered that corrosion of carbonaceous materials in different aquatic phases in the absence of an irradiation source was caused by interaction of graphite with dissolved oxygen.

Corrosion rates in aqueous solutions under pure oxygen and air atmosphere decrease in the order water > brine-3 > brine-2 for the described conditions. It was suggested that this effect is connected with different oxygen solubility in the aqueous phases used: the highest corrosion rate of graphite and pyrocarbon in water in the presence of oxygen is related to better oxygen solubility in pure water than in concentrated saline solutions. However, the oxygen in the final repository will be consumed by reacting with iron containers in which the spent fuel is stored. In the absence of oxygen no further graphite corrosion is expected.

In the final repository, the aqueous phase would be irradiated by spent fuel elements and therefore oxidising reagents, formed due to the radiolysis process, will be present. Here the opposite dependence of corrosion rate on the aquatic media was observed. In comparison with experiments without γ -irradiation, the highest corrosion rates were obtained in brines under γ -irradiation, showing the dramatic impact on the carbon material stability in highly concentrated chloride solutions. The corrosion rates of graphite and pyrocarbon in irradiated brine-2 and brine-3 in argon atmosphere were two orders of magnitude higher than in pure oxygen atmosphere in the absence of irradiation. This was considered to be connected with the formation of highly oxidising chlorine species in brines, which react with carbon materials. The SEM investigations of the surface of intact BISO and TRISO particles and the graphite massive sample showed evident marks of uniform corrosion after two months of experiment. The surface of the materials became rougher. In pure water radiolysis did not significantly influence the oxidation process. The corrosion rate was similar to that in oxygen atmosphere.

The irradiation dose rates used in present experiments were very conservative with respect to final repository conditions. Therefore further investigations of graphite and pyrocarbon corrosion as a function of dose rate are required.

The second objective of the present work was devoted to the treatment of contaminated graphite with respect to waste management. The main problem associated with direct disposal

of contaminated graphite is its large volume. Reprocessing of the graphite, based on graphite gasification, offers the opportunity to separate the majority of the short-lived isotopes from the graphite, which then could be further reused. The existing reprocessing scheme allows non-volatile and volatile radionuclides to be separated by chemical methods, resulting at the end in the mixture ^{14}C and ^{12}C . The development of a simplified method for graphite purification from ^{14}C would reduce the waste volume and, therefore, diminish the problem of reactor graphite disposal.

In the present work, the release of tritium and ^{14}C during thermal treatment of contaminated graphite from Merlin thermal column and AVR reflector was investigated. The experiments were performed in a flow of argon and water steam in the temperature range of 870–1060°C. Comparison of release rate ratios of volatilised radionuclides ^{14}C and ^3H with release of ^{12}C showed that under all experimental conditions tritium and ^{14}C were released faster than the graphite sample was oxidised.

For tritium the maximum value of the release rate ratio was obtained in experiments with argon atmosphere and increased with temperature. Tritium originates from the activation of lithium impurities present in graphite. It is located on graphite edge planes or between basal sheets. At elevated temperatures tritium started to diffuse from graphite crystals and can be released to the gas phase. Diffusion coefficients for Merlin graphite samples at temperatures of 870, 970 and 1060°C were determined. The activation energy of diffusion process and pre-exponential factor were estimated from an Arrhenius plot. For Merlin graphite the absolute diffusion coefficient can be presented by the equation:

$$D = 10.7 \cdot \exp(-312 \text{ kJ/mol} / RT) \text{ cm}^2/\text{s}$$

The experiments performed allow the conclusion that tritium can be released without significant volatilisation of graphite by oxidation. Diffusion of tritium in different graphite types depends on the operational conditions. Graphite irradiated at higher temperatures (AVR graphite) requires longer times to remove tritium.

For ^{14}C the maximum fractional release ratio (^{14}C to ^{12}C) was observed for lower temperatures in experiments with water steam as well as in experiments with argon. The difference in release rates of ^{14}C and ^{12}C allows us to assume that ^{14}C is not distributed uniformly in the graphite lattice. Otherwise the normalised release rate of ^{14}C and ^{12}C would be the same. As is known, ^{14}C mainly formed by an (n,p) reaction of nitrogen impurities and from nitrogen impurities adsorbed from the cooling gas, is embedded in the graphite lattice under irradiation conditions. The results of experiments performed indicate that ^{14}C mainly locates near grain boundary surface and its concentration profile decreases with depth. This part of ^{14}C can be released from graphite using low temperature oxidative treatment without significant mass loss.

The behaviour of ^{60}Co , $^{154,155}\text{Eu}$, $^{134,137}\text{Cs}$ and ^{133}Ba , which are present in contaminated graphite, was also investigated. It was shown that during treatment in inert and oxidising atmosphere these radionuclides, beside Cs, remain mainly in the reaction ceramic boat. During heating at high temperatures Cs can diffuse from graphite sample and later be volatilised into the gas phase.

Separated from the main graphite mass tritium, ^{14}C , and other radionuclides can be collected in concentrated form and handled separately. ^{14}C and ^3H could be later reused for commercial purposes (for example as tracers). ^{14}C also can be converted to carbonates or carbon for disposal with a smaller volume than the original graphite.

This work showed the possibility of depleting the ^{14}C inventory in nuclear graphite by thermal treatment. The separation of radioactive carbon allows the problem of radioactive waste

volume to be reduced significantly. However, further investigations are necessary before the process can be developed to a pilot scale.

F. Acknowledgement

I would like to thank Professor Reinhard Odoj, who agreed on supervising this thesis and its promotion at the Aachen University.

I am also grateful to Dr. Johannes Fachinger for supervising my work, numerous helpful suggestions, valuable remarks and proofreading.

I express my sincere acknowledgements to my friends and colleagues Dr. Andrey Bukaemskiy and Maxim Titov for their contribution in idea development, devoting their time for proofreading and continuous support during all my work.

I would like to thank all my colleagues for their help in different ways, especially Rudolf Enge for his assistance throughout the experiments with radioactive materials, Ferdinand Kreutz, Manfred Thome and DIDO team for the organization of the irradiation experiments, Dr. Hilde Curtius for solving everyday problems and helpful advises, Sigfried Dix for IT support.

I express my greatest thanks to my parents and all my friends for their help and care.

Finally I would like to thank the European Community for financial support of this work (Projects No. FIKI-CT-2001-00169 and No. FIKI-CT-2000-00020).

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H. Appendix

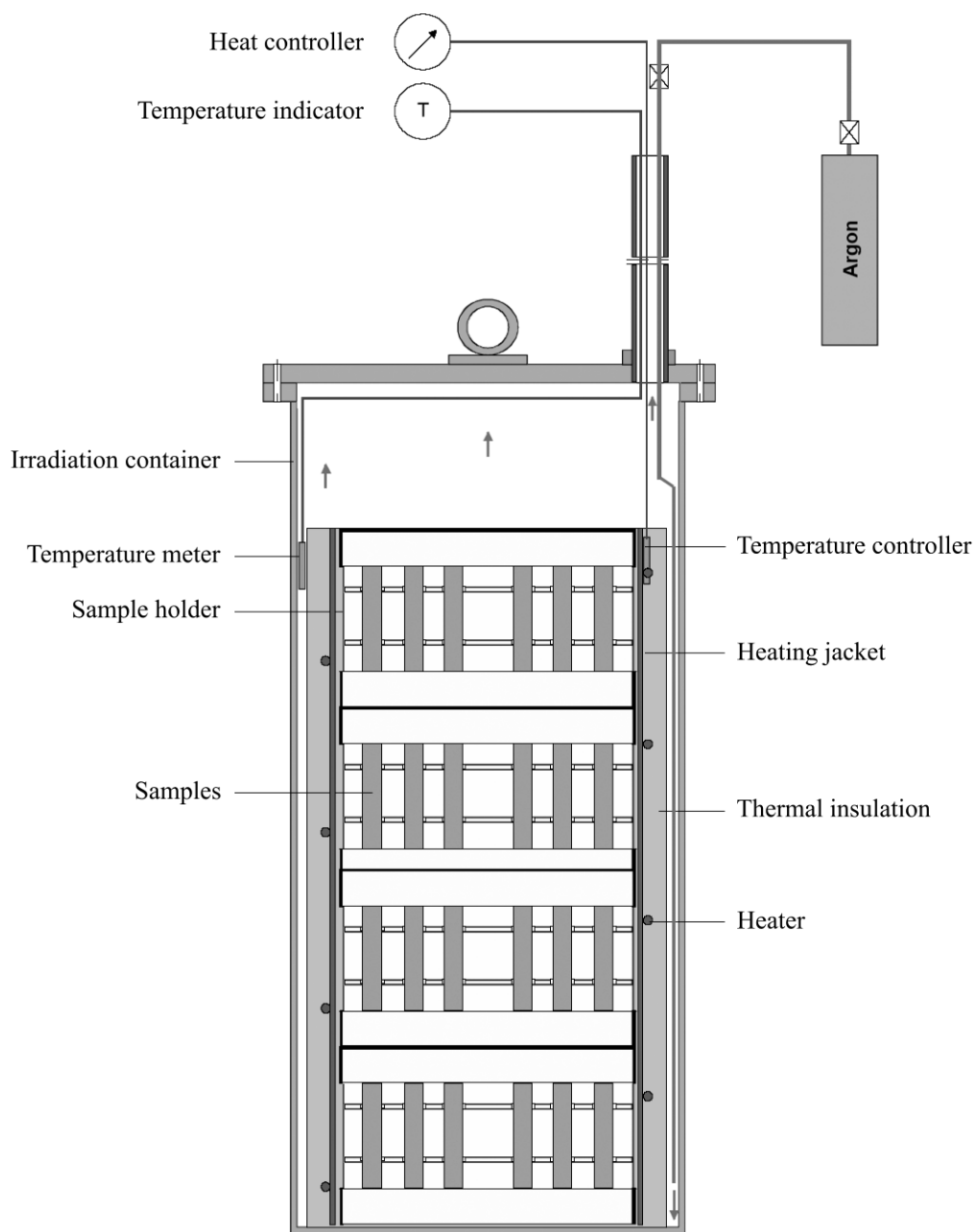


Figure 49. Irradiation container scheme

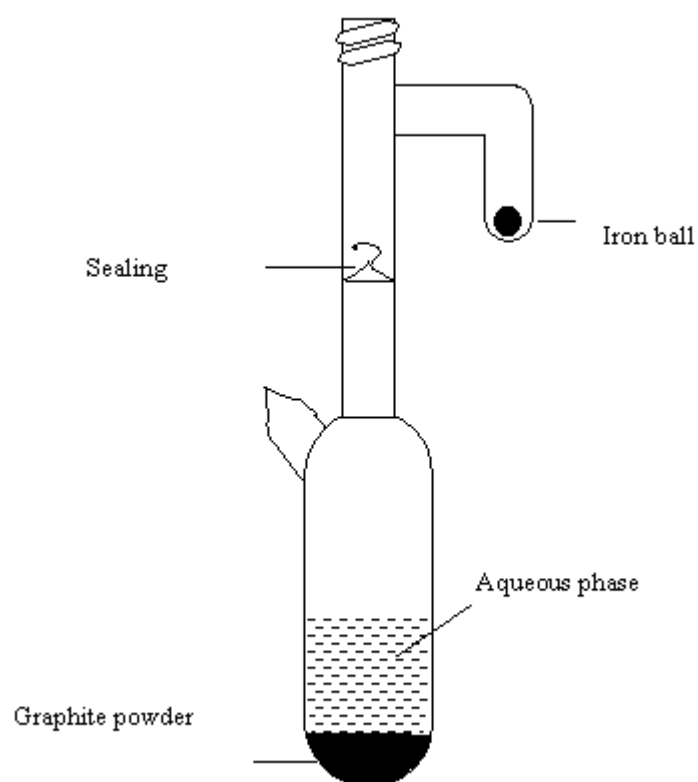


Figure 50. Schematic drawing of the sealed tube

Table 26. Experimental set-up for graphite and pyrocarbon oxidation in the absence of irradiation field

No.	Material	Atmosphere	Liquid phase	Fraction size, mm	Duration, days
1	graphite	argon	brine-2	0.15-0.25	770
2	graphite	argon	brine-2	>0.8	770
3	graphite	argon	brine-2	0.5-0.8	770
4	graphite	argon	brine-2	0.15-0.25	770
5	graphite	argon	brine-2	0.05-0.15	770
6	graphite	argon	brine-2	<0.05	790
7	pyrocarbon	argon	brine-2	—	249
8	pyrocarbon	argon	brine-2	—	249
9	pyrocarbon	argon	brine-2	—	249
10	graphite	argon	water	<0.05	137
11	graphite	argon	water	<0.05	137
12	graphite	oxygen	brine-2	<0.05	92
13	graphite	oxygen	brine-2	<0.05	92
14	graphite	oxygen	brine-2	<0.05	233
15	graphite	oxygen	brine-2	<0.05	240
16	graphite	oxygen	brine-3	<0.05	121
17	graphite	air	brine-2	<0.05	50
18	graphite	air	brine-2	<0.05	101
19	graphite	air	brine-2	0.15-0.25	50
20	graphite	air	brine-2	0.15-0.25	101
21	graphite	air	brine-3	0.15-0.25	55
22	graphite	air	brine-3	0.15-0.25	101
23	graphite	air	brine-3	<0.05	121
24	graphite	oxygen	water	<0.05	55
25	graphite	oxygen	water	<0.05	55
26	graphite	oxygen	water	<0.05	101
27	graphite	oxygen	water	<0.05	101
28	graphite	oxygen	water	<0.05	126
29	graphite	air	water	<0.05	55
30	graphite	air	water	0.15-0.25	101
31	graphite	air	water	<0.05	126
32	pyrocarbon	oxygen	brine-2	—	127
33	pyrocarbon	air	brine-2	—	127
34	pyrocarbon	oxygen	water	—	127
35	pyrocarbon	air	water	—	127

Table 27. Gas phase composition in the experiments with graphite and pyrocarbon under argon atmosphere in brine-2 and water

Nr.	Material	Atmosphere	Liquid phase	O ₂ , vol. %	N ₂ , vol. %	CO ₂ , vol. %	CO, vol. %	Mass, g	Time, days	P, atm
1	graphite	argon	brine-2	-	0.78	0.12	-	1	770	1.1
2	graphite	argon	brine-2	-	0.57	0.05	-	1	770	1.1
3	graphite	argon	brine-2	18.89	76.56	<0.03	-	1	770	1.1
4	graphite	argon	brine-2	0.35	1.78	0.13	-	1	770	1.1
5	graphite	argon	brine-2	0.15	0.74	0.16	-	1	770	1.1
6	graphite	argon	brine-2	<0.15	0.36	0.2	-	1	790	1.1
7	pyrocarbon	argon	brine-2	0.26	0.98	0.01	-	1	249	0.9
8	pyrocarbon	argon	brine-2	0.21	0.91	0.04	-	1	249	0.9
9	pyrocarbon	argon	brine-2	-	-	0.11	-	1	249	0.9
10	graphite	argon	water	0.18	1.15	0.1	-	1	137	0.9
11	graphite	argon	water	0.43	1.57	0.01	-	1	137	0.9

Table 28. Gas phase composition in the experiments with graphite and pyrocarbon coatings under oxygen and air atmosphere in brines and water

Nr.	Material	Atmosphere	Liquid phase	O ₂ , vol. %	N ₂ , vol. %	CO ₂ , vol. %	CO, vol. %	Mass, g	Time, days	P, atm
12	graphite	oxygen	brine-2	98.89	0.34	0.46	-	1	92	0.9
13	graphite	oxygen	brine-2	96.41	0.94	0.84	-	2	92	0.9
14	graphite	oxygen	brine-2	81.14	6.99	0.52	0.09	1	233	0.9
15	graphite	oxygen	brine-2	92	1	1.26	0.15	2	240	0.9
16	graphite	oxygen	brine-3	93.72	1.13	1.12	0	1	121	0.9
17	graphite	air	brine-2	20.52	70.88	0.14	0.006	1	50	0.9
18	graphite	air	brine-2	20.3	71.24	0.09	-	1	50	0.9
19	graphite	air	brine-2	19.84	70.09	0.2	0.01	1	101	0.9
20	graphite	air	brine-2	19.9	70.44	0.4	0.03	1	101	0.9
21	graphite	air	brine-3	19.59	70.26	0.13	0.006	1	55	0.9
22	graphite	air	brine-3	19.92	69.57	0.34	0.03	1	101	0.9
23	graphite	air	brine-3	18.34	68.38	0.51	0.05	1	121	0.9
24	graphite	oxygen	water	93.32	1.94	0.64	0.04	1	55	0.9
25	graphite	oxygen	water	94.02	1.41	0.71	0.04	1	55	0.9
26	graphite	oxygen	water	95.63	1.03	1.08	0.09	1	101	0.9
27	graphite	oxygen	water	91.67	0.96	1.02	0.09	1	101	0.9
28	graphite	oxygen	water	91.79	1.34	1.8	0.08	1	126	0.9
29	graphite	air	water	19.94	69.49	0.18	0.05	1	55	0.9
30	graphite	air	water	19.9	70.24	0.41	0.04	1	101	0.9
31	graphite	air	water	17.54	68.13	0.9	0.01	1	126	0.9
32	pyrocarbon	oxygen	brine-2	94.85	1.3613	0.05	0.03	1	127	0.9
33	pyrocarbon	air	brine-2	19.82	70.62	0.1	0.09	1	127	0.9
34	pyrocarbon	oxygen	water	87.62	1.21	0.2	0.07	1	127	0.9
35	pyrocarbon	air	water	19.96	71.04	0.13	0.08	1	127	0.9

Table 29. Graphite oxidation with hydrogen peroxide (fraction size 0.05–0.15 mm). Gas composition of the glass vessels

Liquid phase	H₂O₂, mol/L	CO₂, vol.%	CO, vpm	O₂, vol.%	N₂, vol.%	Pressure, atm
brine-2	1.07E-03	0.02	-	0.57	0.66	1.72
brine-2	1.07E-03	0.02	-	0.82	0.57	1.88
brine-2	1.07E-02	0.11	-	9.42	2.36	1.75
brine-2	1.07E-02	0.17	-	8.66	1.52	1.61
brine-2	2.14E-02	0.14	-	17.44	4.32	1.88
brine-2	2.14E-02	0.16	-	17.17	1.89	1.75
brine-2	3.21E-02	0.15	-	21.89	1.22	2.10
brine-2	3.21E-02	0.20	-	26.81	1.45	1.83
brine-2	5.35E-02	0.15	-	33.32	0.83	2.45
brine-2	1.07E-01	0.13	-	45	2.11	3.49
brine-2	1.07E-01	0.16	-	49.8	1.8	2.90
brine-2	2.68E-01	0.09	-	70.1	0.34	5.59
brine-2	2.68E-01	0.10	-	69.9	0.59	5.64
water	1.07E-03	0.07	-	0.99		2.02
water	1.07E-03	0.08	-	0.95		1.88
water	1.07E-02	0.52	-	7.66	1.09	2.15
water	1.07E-02	0.57	-	9.37	2.82	1.88
water	2.14E-02	0.90	132	16.06	1.27	2.10
water	2.14E-02	0.88	48	15.78	1.71	2.15
water	3.21E-02	0.89	207	20.73	2.03	2.42
water	3.21E-02	0.99	122	24.16	1.63	2.20
water	5.35E-02	0.99	449	30.7	1.9	2.69
water	5.35E-02	1.08	493	35.1	2.45	2.28
water	1.07E-01	0.99	194	47	2.74	3.31
water	1.07E-01	0.90	595	48.5	1.11	3.36
water	1.61E-01	0.95	223	60.3	1.58	3.70
water	1.61E-01	0.90	657	57.5	1.75	3.90
water	2.68E-01	0.77	272	71	0.39	4.35
water	2.68E-01	0.75	526	70.5	0.45	4.78
blank water	2.68E-01	0.03	-	67.3	0.72	4.90
blank water	2.68E-01	0.03	-	60.9	0.85	5.00
brine-2 blank	2.68E-01	0.01	-	68.5	1.1	5.21
brine-2 blank	2.68E-01	0.05	-	63	0.53	4.87

Table 30. Gas phase composition in the experiments with of graphite (fraction size 0.05–0.015 mm) and pyrocarbon coatings under γ -irradiation in brine-2 and brine-3

Nr.	Sample	Liquid phase	O ₂ , vol. %	H ₂ , vol. %	N ₂ , vol. %	CO ₂ , vol. %	CO, vol. %	Mass, g	Time, days	P, atm	Dose, MGy
γ 1	graphite	brine-2	2.55	44.5	-	17.1	-	1	58	1.8	2.2
γ 2	graphite	brine-2	2.86	44.1	2.4	17.0	-	1	58	2.0	2.2
γ 3	graphite	brine-2	1.61	46.5	0.6	23.7	0.12	1	114	2.6	4.2
γ 4	graphite	brine-2	2.17	46.2	0.4	23.3	0.13	1	114	2.6	4.2
γ 5	graphite	brine-2	2.51	45.4	0.6	24.9	0.14	1	161	2.9	5.3
γ 6	graphite	brine-2	2.08	45.2	0.6	24.8	-	1	161	2.8	5.3
γ 7	graphite	brine-2	2.00	43.7	1.8	21.0	0.11	1	114	1.9	3.3
γ 8	graphite	brine-2	2.07	44.0	1.6	21.1	0.12	1	114	2.0	3.3
γ 9	graphite *	brine-2	5.35	15.9	2.9	2.9	-	0.106	56	1.1	2.0
γ 10	pyrocarbon	brine-2	2.70	40.1	-	13.6	-	1	58	1.7	2.2
γ 11	graphite	brine-3	6.00	39.6	0.6	10.5	-	1	58	1.4	2.2
γ 12	graphite	brine-3	6.14	37.4	3.5	10.2	-	1	58	1.4	2.2
γ 13	graphite	brine-3	2.92	45.9	0.7	14.7	0.17	1	114	1.9	4.2
γ 14	graphite	brine-3	6.25	43.3	3.7	15.8	0.16	1	161	2.0	5.3
γ 15	blank	brine-2	11.13	41.4	-	-	-	1	58	1.4	2.2
γ 16	blank	brine-2	11.30	40.0	2.6	-	-	1	58	1.4	2.2
γ 17	blank	brine-2	17.71	40.4	2.4	-	-	1	161	1.6	5.3
γ 18	blank	brine-3	15.60	35.0	-	0.17	-	1	58	1.3	2.2
γ 19	blank	brine-3	14.76	33.1	-	0.18	-	1	58	1.2	2.2

Table 31. Gas phase composition in the experiments with graphite (fraction size 0.05–0.15 mm) and pyrocarbon under γ -irradiation in water

Nr.	Sample	Liquid phase	O ₂ , vol. %	H ₂ , vol. %	N ₂ , vol. %	CO ₂ , vol. %	CO, vol. %	Mass, g	Time, days	P, atm	Dose, MGy
γ 20	graphite	water	5.01	23.6	3.6	5.1	-	1	58	1.0	2.2
γ 21	graphite	water	2.1	1.6	6.7	0.65	-	1	58	0.7	2.2
γ 22	graphite	water	0.33	2.2	2.5	0.17	-	1	114	0.7	4.2
γ 23	graphite	water	0.56	2.7	2.9	0.22	-	1	114	0.7	4.2
γ 24	graphite	water	2.71	1.8	10.3	0.22	-	1	161	0.8	5.3
γ 25	graphite	water	1.79	2.3	8.4	0.13	-	1	161	0.7	5.3
γ 26	graphite	water	5.72	10.7	2.9	0.26	-	0.2085	56	1.0	2.0
γ 27	Pyrocarbon	water	0.65	2.9	0.4	0.88	-	1	58	0.7	2.2
γ 28	Pyrocarbon	water	1.19	3.5	2.7	1.09	-	1	58	0.7	2.2
γ 29	blank	water	5.7	8.3	4.7	-	-	1	58	0.8	2.2
γ 30	blank	water	6.42	9.3	5.8	-	-	1	58	0.8	2.2
γ 31	blank	water	8.82	16.6	3.5	-	-	1	161	0.8	5.3
γ 32	blank	water	25.93	13.47	-	-	-	1	161	0.8	5.3

Table 32. Gas composition in the experiments with intact coated particles under γ -irradiation in brines and water

Nr.	Sample	Liquid phase	O ₂ , vol. %	H ₂ , vol. %	N ₂ , vol. %	CO ₂ , vol. %	CO, vol. %	Mass, g	Time, days	P, atm	Dose, MGy
γ 33	TRISO	brine-2	9.08	36.32	3.57	1.26	–	0.1087	23	0.95	0.97
γ 34	TRISO	brine-2	8.06	30.17	4.39	1.33	–	0.1177	23	0.95	0.97
γ 35	TRISO	water	2.63	1.12	9.96	–	–	0.11	23	0.72	0.97
γ 36	TRISO	water	2.44	0.99	9.49	–	–	0.1131	23	0.60	0.97
γ 37	TRISO	brine-3	10.35	20.79	4.88	0.49	–	0.1142	23	0.83	0.97
γ 38	TRISO	brine-3	10.23	20.59	6.15	0.47	–	0.1065	23	0.83	0.97
γ 39	BISO	brine-2	7.68	30.1	3.67	1.35	–	0.1041	23	0.98	0.97
γ 40	BISO	brine-2	–	–	–	1.25	–	0.1034	23	0.95	0.97
γ 41	BISO	water	0.27	0.11	0.9	–	–	0.1066	23	0.60	0.97
γ 42	blank	brine-3	9.89	19.76	6.49	0.41	–	–	23	0.86	0.97

Table 33. Characteristics of coated particles

Particle type	Mass of particle, mg	Mass of kernel, mg	Particle diameter, mm	d outer PyC layer, μ m
TRISO	1.81	1.01	1.01	35
BISO	0.64	0.35	0.74	107

Table 34. Tritium and ^{14}C release from Merlin graphite massive sample, 870°C, argon

M_0 , g	Inventory ^3H , Bq	Inventory ^{14}C , Bq				
1.3644	20782	536				
Time hours	^3H as triated H_2O Bq	^3H as triated H_2 Bq	Mass loss g	Time hours	^{14}C Bq	Mass loss g
0.16	100	79	2.29E-05	0.16	–	2.29E-05
0.83	210	167	1.18E-04	0.83	–	1.18E-04
2.16	302	252	3.09E-04	2.16	–	3.09E-04
3.41	351	291	4.89E-04	3.41	13.2	4.89E-04
4.66	382	305	6.68E-04	4.66	12.3	6.68E-04
6.16	428	339	8.82E-04	6.16	14.0	8.82E-04
7.16	465	374	1.03E-03	7.16	16.0	1.03E-03
8.15	488	394	1.17E-03	8.15	19.4	1.17E-03
9.32	501	415	1.34E-03	9.32	18.7	1.34E-03
10.57	535	417	1.51E-03	10.57	19.3	1.51E-03
13.00	576	445	1.86E-03	13.00	25.2	1.86E-03
14.89	604	473	2.13E-03	14.89	26.1	2.13E-03
16.89	639	498	2.42E-03	16.89	28.1	2.42E-03
18.14	652	508	2.60E-03	18.14	29.1	2.60E-03

Table 35. Tritium and ^{14}C release from Merlin graphite powder sample, 970°C, argon

M_0 , g	Inventory ^3H , Bq	Inventory ^{14}C , Bq				
0.4023	3704	235				
Time hours	^3H as triated H_2O Bq	^3H as triated H_2 Bq	Mass loss g	Time hours	^{14}C Bq	Mass loss g
0.67	90	30	4.91E-05	0.67	—	4.91E-05
1.08	124	47	7.98E-05	1.08	—	7.98E-05
1.67	143	55	1.23E-04	1.67	—	1.23E-04
3.00	204	70	2.21E-04	3.00	—	2.21E-04
4.25	240	80	3.13E-04	4.25	—	3.13E-04
5.17	263	87	3.80E-04	5.17	—	3.80E-04
6.17	275	93	4.54E-04	6.17	—	4.54E-04
7.17	293	95	5.28E-04	7.17	6.1	5.28E-04
8.17	306	100	6.01E-04	8.17	5.7	6.01E-04
9.00	319	104	6.63E-04	9.00	6.0	6.63E-04

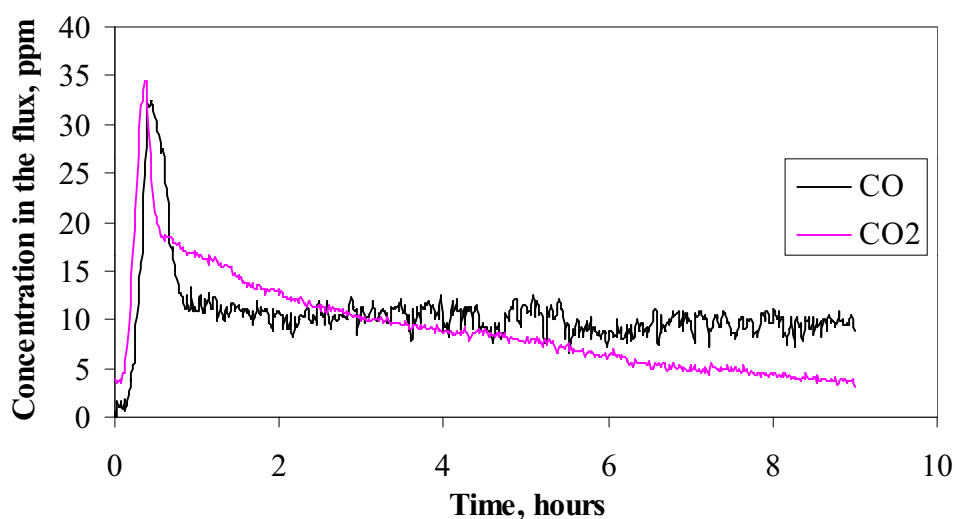


Figure 51. CO and CO_2 concentration in the outlet of carrier gas, Merlin graphite powder sample, 970°C, argon

Table 36. Tritium and ^{14}C release from Merlin graphite powder sample, 1060°C, argon

M_0 , g	Inventory ^3H , Bq	Inventory ^{14}C , Bq				
0.15	1487	89.6				
Time hours	^3H as triated H_2O Bq	^3H as triated H_2 Bq	Mass loss g	Time hours	^{14}C Bq	Mass loss g
0.33	32	48	1.14E-04	0.83	—	1.14E-04
0.82	42	98	1.80E-04	1.32	—	1.80E-04
1.33	55	129	2.51E-04	1.83	—	2.51E-04
1.82	76	145	3.17E-04	2.32	—	3.17E-04
2.35	95	157	3.90E-04	2.85	3.4	3.90E-04
3.83	124	192	5.93E-04	4.33	4.5	5.93E-04
5.83	164	234	8.66E-04	6.33	5.9	8.66E-04
7.83	201	250	1.14E-03	8.33	7.3	1.14E-03
9.42	232	263	1.37E-03	9.92	10.0	1.37E-03
10.92	258	282	—	10.92	—	—
11.97	267	300	1.49E-03	11.97	14.8	1.49E-03
13.18	275	318	1.64E-03	13.18	17.1	1.64E-03
13.98	283	330	1.91E-03	13.98	16.9	1.91E-03
14.92	291	341	2.04E-03	14.92	18.3	2.04E-03

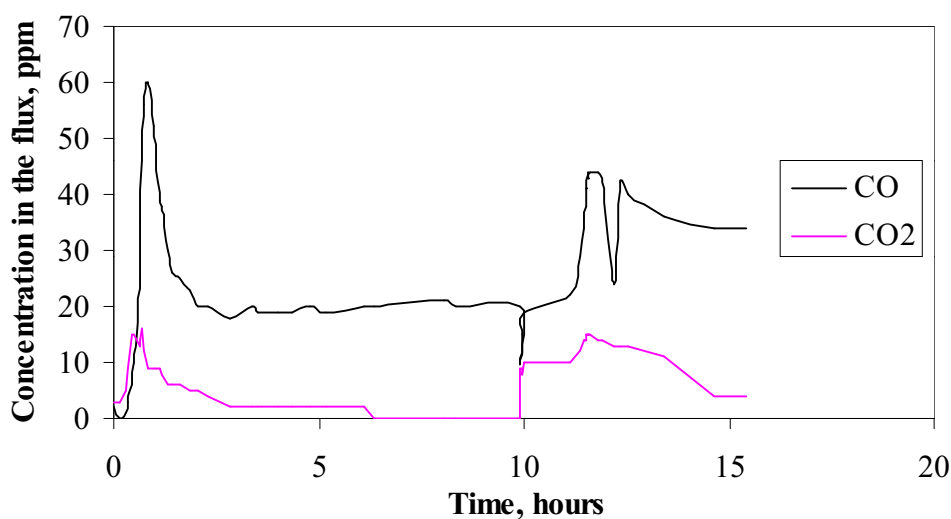


Figure 52. CO and CO₂ concentration in the outlet of carrier gas, Merlin graphite powder sample, 1050°C, argon

Table 37. Tritium and ^{14}C release from Merlin graphite massive sample, 1060°C, argon

M_0 , g	Inventory ^3H , Bq	Inventory ^{14}C , Bq				
0.9116	11446	531				
Time hours	^3H as triated H_2O Bq	^3H as triated H_2 Bq	Mass loss g	Time hours	^{14}C Bq	Mass loss g
0.50	372	373	1.36E-04	0.50	—	1.36E-04
1.00	611	727	2.71E-04	1.00	9.2	2.71E-04
1.50	748	965	4.06E-04	1.50	12.7	4.06E-04
2.17	869	1142	5.86E-04	2.17	16.4	5.86E-04
3.34	1032	1393	9.01E-04	3.34	23.2	9.01E-04
4.84	1202	1636	1.31E-03	4.84	30.6	1.31E-03
5.92	1294	1807	1.60E-03	5.92	36.8	1.60E-03
7.99	1426	1981	2.16E-03	7.99	41.5	2.16E-03
11.24	1610	2202	3.03E-03	11.24	50.8	3.03E-03
13.40	1698	2331	3.62E-03	13.40	56.8	3.62E-03

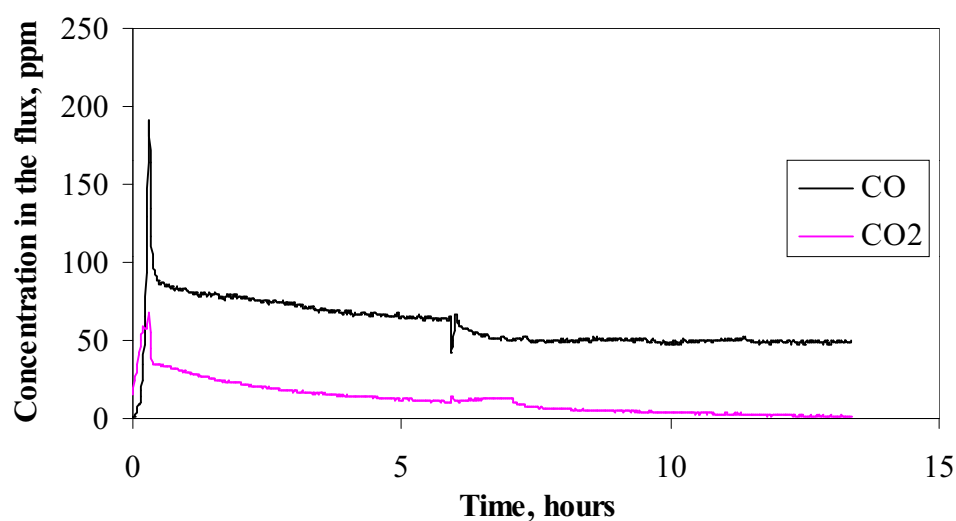


Figure 53. CO and CO₂ concentration in the outlet of carrier gas, Merlin graphite massive sample, 1060°C, argon

Table 38. Tritium and ^{14}C release from AVR graphite powder sample, 1060°C, argon

M_0 , g	Inventory ^3H , Bq	Inventory ^{14}C , Bq				
0.213	363649	25249				
Time hours	^3H as triated H_2O Bq	^3H as triated H_2 Bq	Mass loss g	Time hours	^{14}C Bq	Mass loss g
0.66	11648	12824	1.17E-04	0.66	91	1.17E-04
1.67	23807	20901	2.94E-04	1.67	383	2.94E-04
2.67	29675	23096	4.70E-04	2.67	631	4.70E-04
3.67	34066	24977	6.46E-04	3.67	847	6.46E-04
4.67	37782	26377	8.23E-04	4.67	1032	8.23E-04
6.67	44163	29403	1.18E-03	6.67	1339	1.18E-03
7.83	47026	30294	1.38E-03	7.83	1522	1.38E-03
10.01	52096	32299	1.77E-03	10.01	1851	1.77E-03
11.01	54260	33229	1.94E-03	11.01	1969	1.94E-03
12.51	56641	34480	2.21E-03	12.51	2143	2.21E-03
14.01	59787	35450	2.47E-03	14.01	2317	2.47E-03
15.01	61573	36276	2.65E-03	15.01	2533	2.65E-03

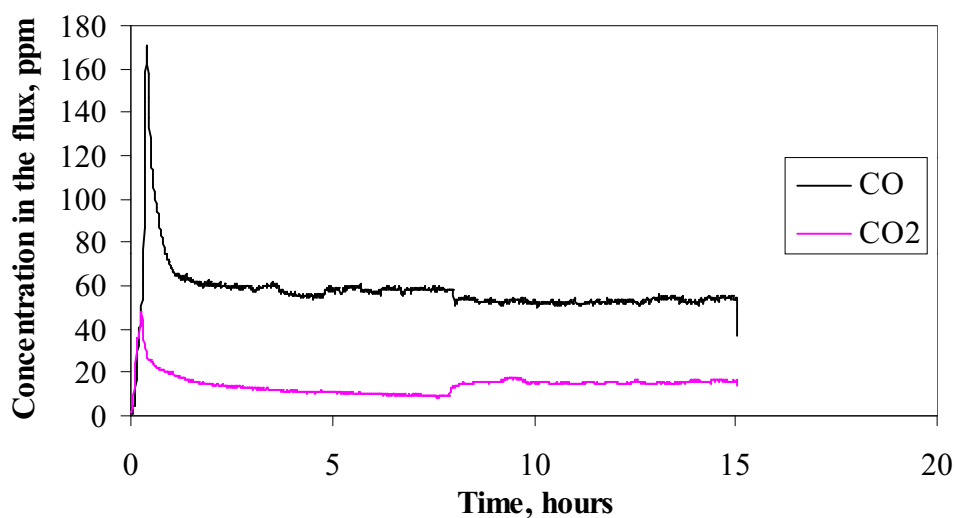


Figure 54. CO and CO_2 concentration in the outlet of carrier gas, AVR graphite powder sample, 1060°C, argon

Table 39. Tritium and ^{14}C release from Merlin graphite powder sample, 960°C, $p_{\text{H}_2\text{O}}$ 7.4 kPa, flow rate 80 mL/min

M_0 , g	Inventory ^3H , Bq	Inventory ^{14}C , Bq				
0.2262	2411	117				
Time hours	^3H as triated H_2O Bq	^3H as triated H_2 Bq	Mass loss g	Time hours	^{14}C Bq	Mass loss g
0.25	153	66	1.96E-04	0.25	—	1.96E-04
0.58	204	136	4.57E-04	0.58	—	4.57E-04
1.33	309	260	1.05E-03	1.33	—	1.05E-03
2.50	364	374	1.96E-03	2.50	7.1	1.96E-03
3.50	429	460	2.74E-03	3.50	7.7	2.74E-03
4.58	488	555	3.59E-03	4.58	9.7	3.59E-03
5.33	538	—	4.18E-03	5.33	11.6	4.18E-03
6.42	572	635	5.03E-03	6.42	14.3	5.03E-03
7.42	582	708	5.81E-03	7.42	16.2	5.81E-03
8.25	610	754	6.47E-03	8.25	18.0	6.47E-03
9.42	671	871	7.38E-03	9.42	20.3	7.38E-03

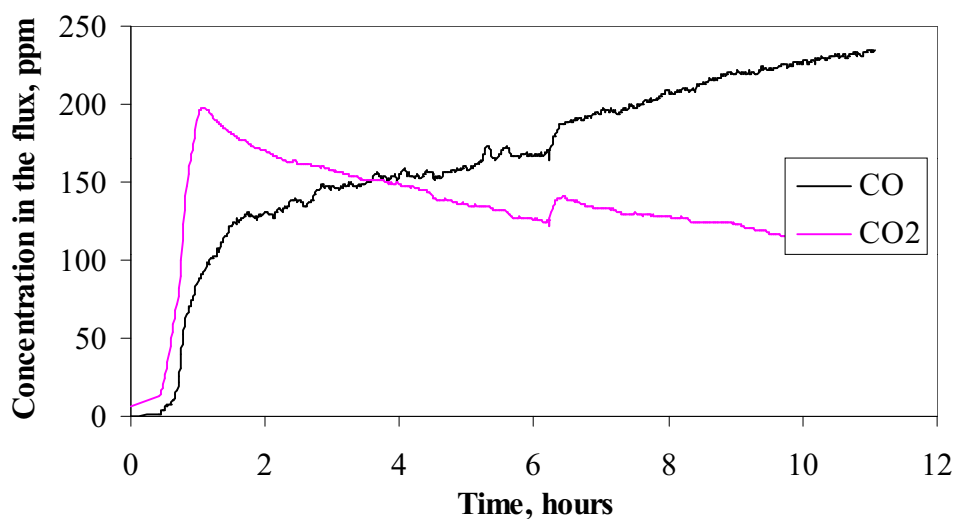


Figure 55. CO and CO₂ concentration in the outlet of carrier gas

Table 40. Tritium and ^{14}C release from Merlin graphite powder sample, 960°C, $p_{\text{H}_2\text{O}}$ 7.4 kPa, flow rate 660 mL/min

M_0 , g	Inventory ^3H , Bq	Inventory ^{14}C , Bq				
0.249	2824	190				
Time hours	^3H as triated H_2O Bq	^3H as triated H_2 Bq	Mass loss g	Time hours	^{14}C Bq	Mass loss g
0.34	255	205	5.24E-04	0.67	—	1.04E-03
0.51	380	277	7.80E-04	1.17	14.3	1.81E-03
0.67	437	327	1.04E-03	2.42	25.2	3.73E-03
1.17	568	447	1.81E-03	3.67	29.1	5.65E-03
1.67	647	555	2.57E-03	4.67	35.3	7.19E-03
2.42	724	652	3.73E-03	5.67	42.8	8.73E-03
3.67	913	815	5.65E-03	6.51	44.6	1.00E-02
6.51	933	1026	1.00E-02	—	—	—

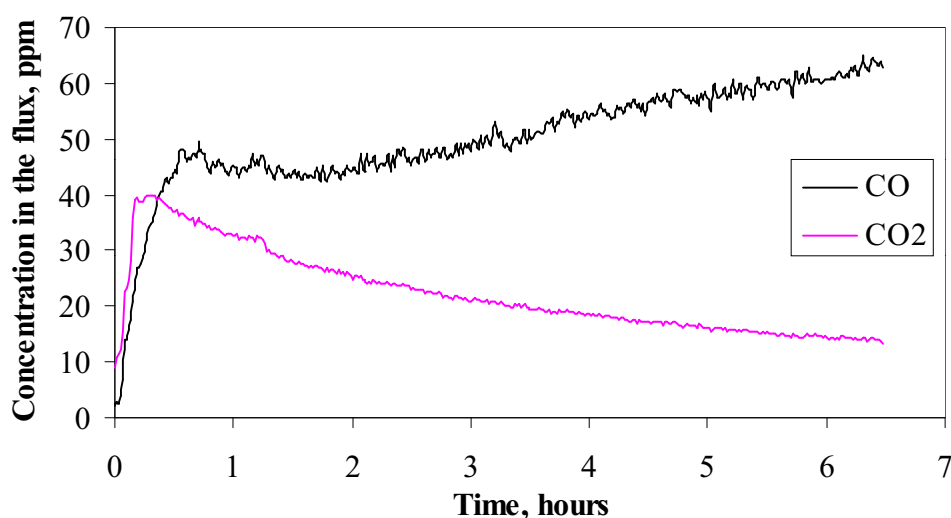


Figure 56. CO and CO₂ concentration in the outlet of carrier gas, Merlin graphite powder sample, 960°C, $p_{\text{H}_2\text{O}}$ 7.4 kPa, flow rate 660 mL/min

Table 41. Tritium and ^{14}C release from Merlin graphite massive sample, 1060°C, $p_{\text{H}_2\text{O}}$ 2.3kPa

M_0 , g	Inventory ^3H , Bq	Inventory ^{14}C , Bq				
0.446	9604	295				
Time hours	^3H as triated H_2O Bq	^3H as triated H_2 Bq	Mass loss g	Time hours	^{14}C Bq	Mass loss g
0.66	22	448	7.89E-03	0.66	20	7.89E-03
0.74	164	1068	8.81E-03	0.82	30	9.76E-03
1.07	604	2033	1.27E-02	1.41	48	1.68E-02
2.41	2190	4610	2.87E-02	2.41	77	2.87E-02
3.41	3294	5994	4.06E-02	3.41	96	4.06E-02
4.41	4293	6914	5.25E-02	4.41	117	5.25E-02
5.52	5011	7789	6.57E-02	5.41	129	6.45E-02
7.09	5895	8682	8.44E-02	6.91	147	8.22E-02
8.24	6157	9038	9.81E-02	8.41	164	1.00E-01
10.07	6302	9383	1.20E-01	10.07	181	1.20E-01
11.41	6372	9498	1.36E-01	11.41	193	1.36E-01
12.94	6435	9498	1.54E-01	12.74	205	1.52E-01
14.74	6371	9658	1.75E-01	16.24	227	1.93E-01
16.24	6338	9577	1.93E-01	17.74	234	2.11E-01
17.74	6327	9577	2.11E-01	18.99	242	2.26E-01
18.99	6277	9550	2.26E-01	20.14	247	2.40E-01
20.14	6277	9550	2.40E-01	21.23	251	2.53E-01
21.23	6277	9550	2.53E-01	22.64	260	2.70E-01
22.64	6277	9550	2.70E-01	24.14	257	2.88E-01
25.24	6277	9550	3.01E-01	25.24	259	3.01E-01

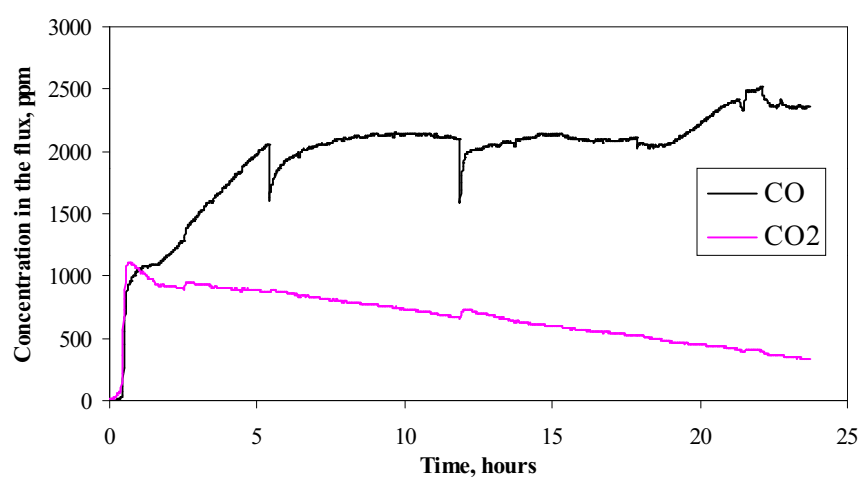


Figure 57. CO and CO_2 concentration in the outlet of carrier gas, from Merlin graphite massive sample, 1060°C, $p_{\text{H}_2\text{O}}$ 2.3kPa

Table 42. Tritium and ^{14}C release from Merlin graphite powder sample, 1050°C, $p_{\text{H}_2\text{O}}$ 2.3 kPa

M_0 , g	Inventory ^3H , Bq	Inventory ^{14}C , Bq				
0.439	3380	262				
Time hours	^3H as triated H_2O Bq	^3H as triated H_2 Bq	Mass loss g	Time hours	^{14}C Bq	Mass loss g
0.73	11	257	7.73E-03	0.73	9.6	7.73E-03
0.98	52	398	1.04E-02	0.98	10.5	1.04E-02
1.56	238	608	1.66E-02	1.56	18.3	1.66E-02
2.39	408	779	2.54E-02	2.39	28.2	2.54E-02
3.39	625	926	3.61E-02	3.39	39.5	3.61E-02
4.48	843	1040	4.76E-02	4.48	51.7	4.76E-02
5.48	1017	1105	5.82E-02	5.48	60.7	5.82E-02
6.14	1178	1152	6.53E-02	6.14	70.1	6.53E-02
7.41	1701	1214	7.97E-02	7.41	83.0	7.97E-02
8.41	1746	1251	8.93E-02	8.41	90.4	8.93E-02
9.41	1764	1302	1.00E-01	9.41	96.7	1.00E-01

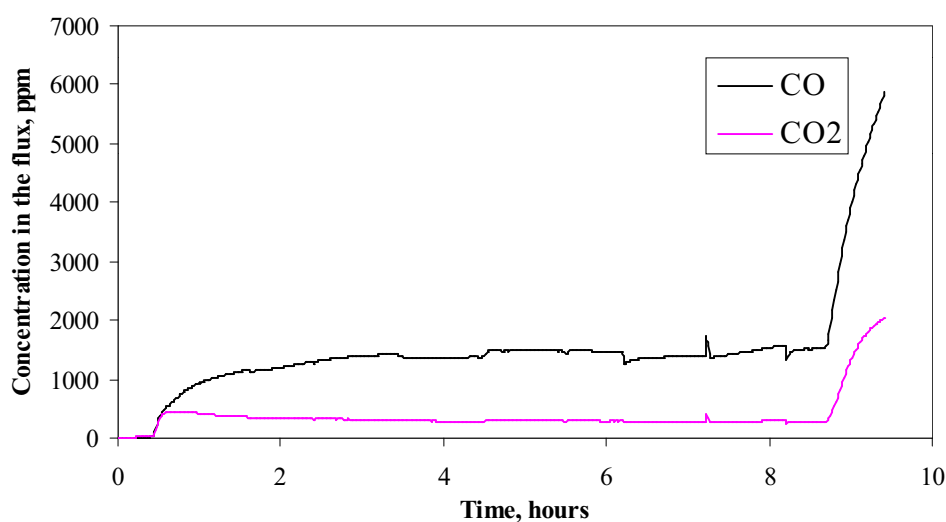


Figure 58. CO and CO₂ concentration in the outlet of carrier gas, Merlin graphite powder sample, 1050°C, $p_{\text{H}_2\text{O}}$ 2.3 kPa

Table 43. Tritium and ^{14}C release from Merlin graphite powder sample, 1060°C, $p_{\text{H}_2\text{O}}$ 7.4 kPa, flow rate 660 mL/min

M_0 , g	Inventory ^3H , Bq	Inventory ^{14}C , Bq				
0.239	1993	152				
Time hours	^3H as triated H_2O Bq	^3H as triated H_2 Bq	Mass loss g	Time hours	^{14}C Bq	Mass loss g
0.17	265	188	1.57E-03	0.17	5.8	1.57E-03
0.33	399	281	3.14E-03	0.33	9.5	3.14E-03
0.50	466	343	4.71E-03	0.50	12.9	4.71E-03
1.00	621	466	9.42E-03	1.00	18.9	9.42E-03
2.00	786	607	1.88E-02	2.00	29.7	1.88E-02
5.00	940	778	4.71E-02	3.00	42.5	2.83E-02
6.00	918	802	5.65E-02	4.00	50.2	3.77E-02
7.00	911	820	6.60E-02	5.00	59.4	4.71E-02
8.00	909	834	7.54E-02	8.00	94.9	7.54E-02
9.00	—	—	—	9.00	100.7	8.48E-02
10.00	—	—	—	10.00	107.6	9.42E-02
11.00	—	—	—	11.00	113.0	1.04E-01

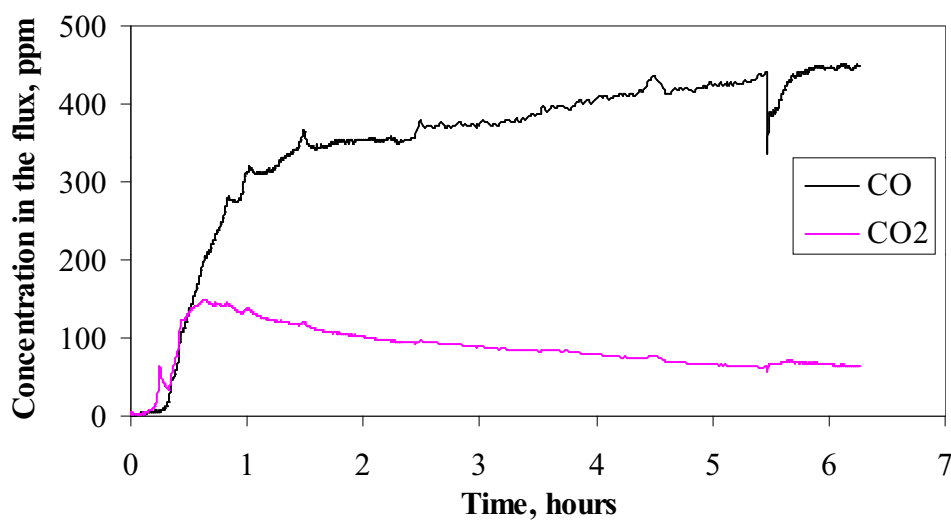


Figure 59. CO and CO₂ concentration in the outlet of carrier gas, Merlin graphite powder sample, 1060°C, $p_{\text{H}_2\text{O}}$ 7.4 kPa, flow rate 660 mL/min

Table 44. Tritium and ^{14}C release from AVR graphite powder sample, 1060°C, 2.3 kPa

M_0 , g	Inventory ^3H , Bq	Inventory ^{14}C , Bq			
0.087	142276	11414			
Time, hours	^3H , as triated water, Bq	^3H , as triated hydrogen, Bq	Time, hours	^{14}C , Bq	Mass loss, g
0.91	13076	3068	0.91	472	8.22E-04
1.91	20279	5074	1.91	947	1.73E-03
2.91	24386	6702	2.91	1348	2.63E-03
3.91	28930	7930	3.91	1748	3.53E-03
4.91	30175	8841	4.91	2063	4.44E-03
5.91	32931	9449	5.91	2293	5.34E-03
6.91	35064	10466	6.91	2577	6.24E-03
7.91	36441	11174	7.91	2806	7.15E-03
9.49	38555	12314	9.49	3214	8.58E-03
10.32	43063	12957	10.32	3461	9.33E-03
11.32	43288	13755	11.32	3665	1.03E-02
12.99	44921	14601	12.99	3934	1.17E-02
13.99	45638	15529	13.99	4167	1.26E-02
14.99	46225	16358	14.99	4346	1.35E-02
15.82	46977	16700	15.82	4421	1.43E-02

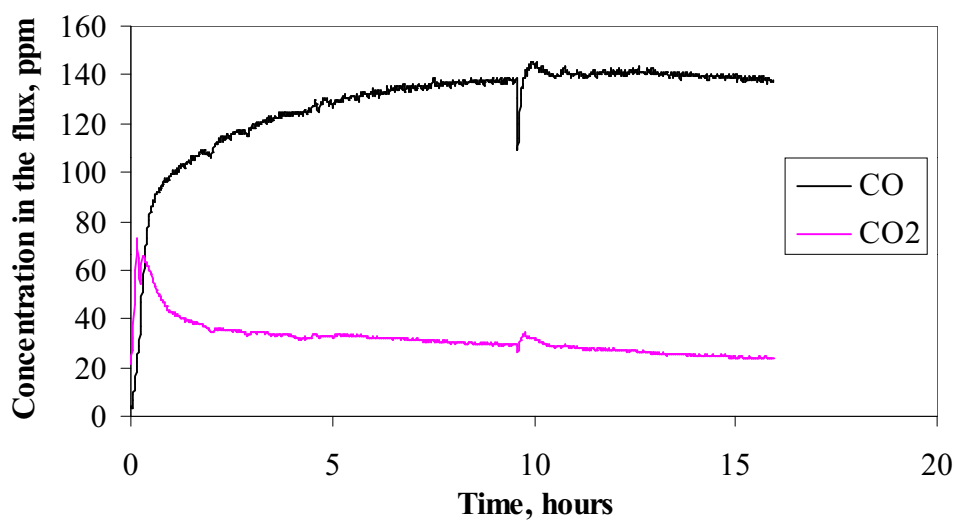


Figure 60. CO and CO₂ concentration in the outlet of carrier gas, AVR graphite powder sample, 1060°C, 2.3 kPa

Table 45. Tritium and ^{14}C release from AVR graphite powder sample, 1060°C, $p_{\text{H}_2\text{O}}$ 31 kPa

M_0 , g	Inventory ^3H , Bq	Inventory ^{14}C , Bq				
0.0726	107057	10006				
Time hours	^3H as triated H_2O Bq	^3H as triated H_2 Bq	Mass loss g	Time hours	^{14}C Bq	Mass loss g
0.54	1520	3068	2.72E-04	0.54	98	2.72E-04
1.54	20470	5074	4.37E-03	1.54	1299	4.37E-03
2.54	29279	6702	8.83E-03	2.54	2089	8.83E-03
4.54	44605	7930	1.74E-02	4.54	3678	1.74E-02
6.54	55536	8841	2.50E-02	6.54	4597	2.50E-02
8.00	61480	9449	3.00E-02	8.00	5354	3.00E-02
10.50	65808	10466	3.69E-02	10.50	6146	3.69E-02
11.60	66333	11174	3.95E-02	11.60	6431	3.95E-02
12.60	68332	12314	4.16E-02	12.60	6529	4.16E-02
13.10	68125	12957	4.26E-02	13.10	6861	4.26E-02

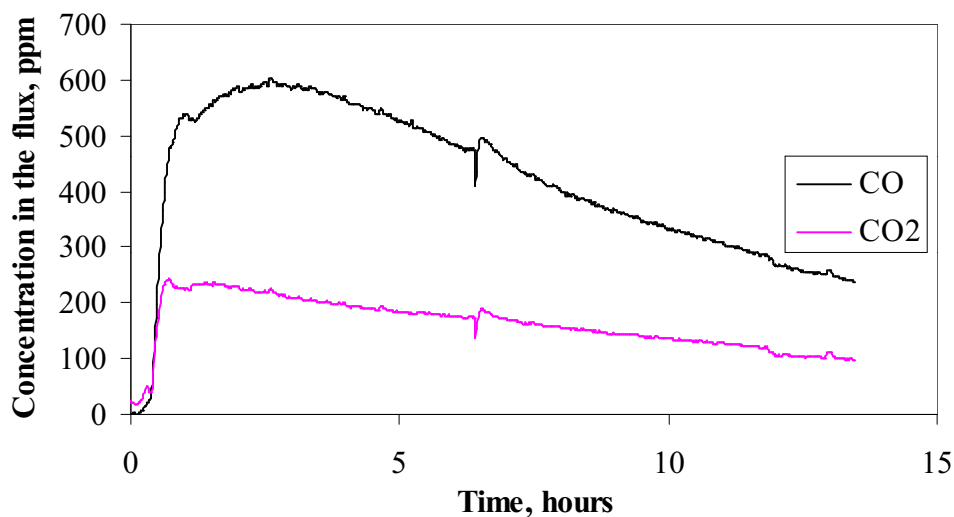


Figure 61. CO and CO₂ concentration in the outlet of carrier gas, AVR graphite powder sample, 1060°C, $p_{\text{H}_2\text{O}}$ 31 kPa

Table 46. Tritium and ^{14}C release from Merlin graphite with stepwise temperature increase by oxidation in water steam at vapor pressure 70 kPa

M ₀ , g	Inventory ³ H, Bq	Inventory ¹⁴ C, Bq	
0.459	3515	289	
Time, hours	T, °C	³ H, Bq	¹⁴ C, Bq
1	400	6	-
2	400	18	-
3	400	36	-
4	400	47	-
5	400	47	-
6	600	47	-
7	600	52	-
8	600	74	-
9	600	90	2
10	600	104	2
11	800	157	41
12	800	215	44
13	800	556	45
14	800	789	48
15	800	1019	49
16	955	1043	114
17	955	1518	180
18	955	2509	221
19	955	3189	240
20	955	3497	265
21	1055	3503	286
22	1055	3513	288
23	1055	3512	289
24	1055	3515	289
25	1055	3515	289

Table 47. γ -analysis of AVR graphite

Sample Nr.	Activity, Bq/g						
	^{60}Co	^{133}Ba	^{134}Cs	^{137}Cs	^{152}Eu	^{154}Eu	^{155}Eu
1	12040	1425	169	3623	<30	632	166
2	14030	1331	202	2421	<30	664	189
3	10693	1431	190	2204	<30	518	148
4	11620	1477	111	4065	<30	522	151
5	13050	1420	230	2252	<30	605	154
6	11921	1385	165	2285	<30	517	138
7	16610	1585	110	2810	<30	564	142
8	17210	1400	180	3157	<30	650	176
Average	13397	1432	170	2852		584	158
Reported data*	18913	653	122	711	80	621	183

* – [93] sample S-GR-5 Nr.1 corrected to time

Table 48. γ -analysis of Merlin graphite

Sample Nr.	Activity, Bq/g						
	^{60}Co	^{133}Ba	^{134}Cs	^{137}Cs	^{152}Eu	^{154}Eu	^{155}Eu
1	413	–	–	0.14	625	56	–
2	569	–	–	0.21	654	61	–
Reported data*	654	410	–	–	820	70	4

* – [94] sample TS10 corrected to time

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Forschungszentrum Jülich
in der Helmholtz-Gemeinschaft



Jül-4166
Februar 2005
ISSN 0944-2952