

Treatment and Disposal of irradiated Graphite and other Carbonaceous Waste

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Einleitung

Die erste Generation von Kernreaktoren nutzt Graphit zur Moderation von Spaltneutronen. Der extrem niedrige Neutroneneinfangquerschnitt von Kohlenstoff erlaubte den Einsatz von nicht-angereichertem Natururan für diesen Reaktortyp. Seit Mitte der 1950er Jahre wurden CO₂-gekühlte und mit Graphit moderierte Reaktoren zur kommerziellen Stromerzeugung errichtet. Hochtemperatur-Reaktoren (HTR), wassergekühlte, graphitmoderierte Reaktoren (RBMK) sowie diverse Forschungs- bzw. Materialtestreaktoren (MTR) verwenden Graphit ebenfalls als Moderator und Neutronenreflektoren. Viele dieser Anlagen sollen nun zurückgebaut werden und benötigen eine Entsorgungsstrategie für bestrahlten Graphit, welcher unterschiedliche Anteile an Radionukliden wie ³H, ¹⁴C, ³⁶Cl, ⁶⁰Co usw. enthält. Dies ist auf Neutronenaktivierung des natürlich vorkommenden ¹³C-Isotops sowie auf Verunreinigungen im Graphit oder im Kühlgas (z.B. Stickstoff) zurückzuführen.

Das europäische Projekt 'Treatment and Disposal of Irradiated Graphite and other Carbonaceous Waste (CARBOWASTE)' wurde in 2008 unter dem 'Siebten Rahmenprogramm der Europäischen Atomgemeinschaft für Forschungs- und Ausbildungsmaßnahmen im Nuklearbereich' begonnen und umfasst Bergung, Charakterisierung, Behandlung, Rezyklierung und Endlagerung von bestrahltem Graphit einschließlich nicht-graphitierter Kohlenstoffwerkstoffe und Pyrokohlenstoff.

Das komplementäre deutsche Projekt 'Entsorgung von bestrahltem Graphit (CarboDISP)' befasst sich seit Ende 2010 mit den speziellen Annahmebedingungen für das deutsche KONRAD Endlager und wird vom Bundesministerium für Bildung und Forschung gefördert. Beide Projekte werden vom Forschungszentrum Jülich koordiniert.

Introduction

The very first generation of nuclear reactors relied on graphite for the moderation of fission neutrons in the core. The extremely low neutron capture cross section of carbon allowed the use of

natural, non-enriched uranium fuel for this type of reactors. Since mid of the 1950s, CO₂-cooled graphite-moderated reactors were built as the first commercial nuclear power stations. High-Temperature Reactors (HTR), water-cooled graphite-moderated reactors (RBMK) as well as diverse Material Test Reactors (MTR) also utilise graphite as moderator and reflector. Many of these facilities are now facing decommissioning and raise the need for the management of irradiated graphite waste, which contains varying fractions of radionuclides including ³H, ¹⁴C, ³⁶Cl, ⁶⁰Co etc., due to neutron activation of the natural ¹³C isotope and of impurities within the graphite or coolant gas (e.g. nitrogen).

The European project on ‘Treatment and Disposal of Irradiated Graphite and other Carbonaceous Waste (CARBOWASTE)’ was launched in 2008 under the 7th EURATOM Framework Programme and addresses the retrieval, characterization, treatment, reuse and disposal of irradiated graphite including other carbonaceous waste such as non-graphitized carbon materials or pyrocarbon.

Since the end of 2010, the complementary German project ‘Disposal of irradiated Graphite (CarboDISP)’ is dealing with the specific requirements for irradiated graphite in the German KONRAD waste repository and is funded by the German Federal Ministry of Education and Research. Both projects are coordinated by the Research Centre Jülich.

1. The Consortium

The CARBOWASTE project is the very first multi-national approach on a European level to federate most organisations dealing with the treatment and disposal of radioactive carbonaceous wastes with the aim to develop an integrated waste management concept as well as innovative processes for treatment and recycling of purified material, as an additional option. CARBOWASTE is also cross-cutting in the sense that it combines two communities, one dealing with legacy waste issues and the other targeting for innovative reactor systems such as Very/High-Temperature Reactors or fusion.

The CARBOWASTE consortium engages 30 partners including many stakeholders with irradiated graphite waste management issues. All European countries being faced with this kind of waste in a larger extent are covered by the consortium.

The CARBOWASTE consortium represents partners from:

- Nuclear industry (AMEC NNC, AREVA NP, Doosan Babcock, FNAG, PBMR)
- Waste management companies (Bradtec, Studsvik)
- Utilities: EDF, SOGIN, (EPRI)
- Graphite manufacturers (GrafTech, SGL-Carbon)
- Waste management authorities (ANDRA, ENRESA, NDA)
- Research (CEA, CIEMAT, ENEA, FTMC, FZJ, INR, JRC, LEI, NNL, NRG, SCK•CEN, NECSA)
- Universities (École de Mines de Nantes, ENS, IPNL, The University of Manchester)

The CARBOWASTE work programme benefits from this complementary multi-disciplinary scientific and industrial background, which is available in the partner organisations from 10 European countries and South Africa. Close connections are established with EPRI to communicate with further international partners.

2. The Objectives

The main objective of the CARBOWASTE project is the development of best practices in the retrieval, characterisation, treatment and disposal of irradiated graphite (i-graphite) including other i-carbonaceous waste like structural material made of graphite or non-graphitised carbon bricks and fuel coatings (pyrocarbon, silicon carbide) [1]. It addresses both existing legacy waste from past and actually operated graphite-moderated reactors as well as waste from carbon-based HTR fuel elements or from the heat-resistant walls of future fusion reactors.

After defining the various targets (end points) for an integrated waste management approach, analysis of the key stages of the road map (i.e. from in-reactor storage to final disposal) can then be undertaken with regard to safe and the most economic, environmental and sustainable options. This methodological approach will enable EU Member States to select the most appropriate options to meet their specific criteria and considerations. Emphasis will therefore be given to legacy i-graphite as this currently represents a significant problem that will have to be addressed, in the short and medium term.

Some Member States and other countries are beginning to evaluate strategies and develop options for the identification, retrieval, characterisation, treatment and final disposal of this waste. It is important that this project takes account of them and assimilates their considerations against appropriate end points. The project unites organisations from most EU Member States being faced with a need for i-carbonaceous waste management (GB, FR, LT, ES, IT, DE, BE, NL, SE, RO). It thus permits quantification of the magnitude of the problem and to identify the most relevant grades and sources of i-carbonaceous waste.

This waste issue has still to be managed for the gas-cooled reactors (Magnox, AGR, UNGG, HTR) and the other graphite-moderated reactors such as RBMK or in Materials Test Reactors (MTR) as well as early production reactors. Irradiated and contaminated graphite from reactor moderators and reflectors or thermal columns, and other related carbonaceous materials, represent the greatest volume of irradiated waste materials from these reactors. Up to now, about 250,000 tons have been accumulated, worldwide. In addition, these reactors have not been designed for decommissioning as can be seen from figure 1, which illustrates the assembly of graphite blocks in a French UNGG reactor. This complex assembling process de facto needs to be reversed, for retrieving the irradiated blocks by remote techniques or shielding to handle the graphite.



Figure 1: Chinon A3 Core Assembly in 1965 (EDF Mediatheque / Brigaud Michel)

A specific problem related to i-carbonaceous waste stemming from the structures of the core is the varying content of long-lived radioisotopes, especially of radiocarbon, resulting from activation processes under neutron irradiation. If other long-lived radioisotopes are present in smaller quantities, their management might also be an important issue because of the particular properties of some of them under disposal conditions like chlorine (^{36}Cl). Dependent on the specific national legislation, they can be a crucial parameter for a final disposal. Therefore, this type of waste is handled as Intermediate-Level Waste (ILW), in some countries, and Long-lived Low-level Waste (LLLW) or as radioactive waste with negligible heat generation, in others. Burning i-graphite has been discussed in the past as an alternative to the disposal option but will most probably not be politically and ecologically accepted due to the radiocarbon releases to the environment if not separated or reduced in the exhaust gas. Recycling or reuse of treated i-graphite in the nuclear industry might be a preferable new option to minimize waste streams for disposal.

The CARBOWASTE consortium has the opportunity to build upon previous work, to review technological advances and innovative ideas, which have arisen in more recent years, and thus to identify the most technologically appropriate, environmentally sustainable, and cost-effective procedures, at all stages in the retrieval, treatment and disposal of all types of carbonaceous wastes.

The previously employed procedures are not necessarily appropriate for the future. The special character of i-graphite wastes can lead to problems such as electrochemical corrosion and the potential leaching of long-lived isotopes if they are handled by the standard methods though appropriate for other wastes. A special issue arises from the fact that radiocarbon (^{14}C) has to be safely isolated from the biosphere due to its biocompatibility. Stored Wigner-Energy is another concern, which has to be addressed especially for graphite being operated at temperatures below about 250°C where significant annealing of radiation effects does not yet take place.

3. The Toolbox

For an integrated waste management approach a set of criteria has been defined, by which options for the retrieval, treatment, recycle and disposal of irradiated graphite can be assessed. This set reflects important aspects of concern in selecting the most sustainable solutions and methods to create a 'toolbox' for graphite waste management [2]. The related criteria have been reviewed to ensure consistency with appropriate EU and international guidelines. They form the basis for a Multi Criteria Decision Analysis (MCDA) framework, which will be used to assess alternate waste management approaches for irradiated graphite.

The first stage of this approach involved an extensive international review of the current state-of-the-art on irradiated graphite management and practical experience. This exercise reviewed current practices; knowledge and ongoing research on this subject, but also helped to identify the knowledge gaps, that would subsequently become the focus of further research work within the CARBOWASTE project. The following projects that represented retrieval experience up to 2009 were reviewed:

- GLEEP Research Reactor Harwell, a low energy graphite pile requiring mechanised handling techniques and shredding of graphite,
- Windscale AGR, a high radioactivity reactor requiring fully remote dismantling of the reactor including several i-graphite removal phases in-air.
- Vandellos 1 silos, that included i-graphite operational wastes (fuel sleeves),
- Fort St Vrain, which represented an under-water decommissioning approach being proposed for graphite moderated reactors such as the UNGG at Bugey,

- Leningrad NPP, which represented RBMK from which i-graphite had been removed during its operational lifetime, and
- The experience at AVR Jülich, where the graphite core has been grouted in-situ.

More recently, i-graphite has been retrieved from a graphite pile at Brookhaven National Laboratory [3] and also by ANSTO in Australia.

The second stage synthesised a range of detailed flowsheet options based on the lifecycle approach, from current in-situ wastes to ultimate recycle/reuse and/or disposal of irradiated graphite including consideration of the stages of retrieval/segregation and potentially in- or ex-situ treatment of the graphite. A simplified lifecycle is illustrated below in figure 2.

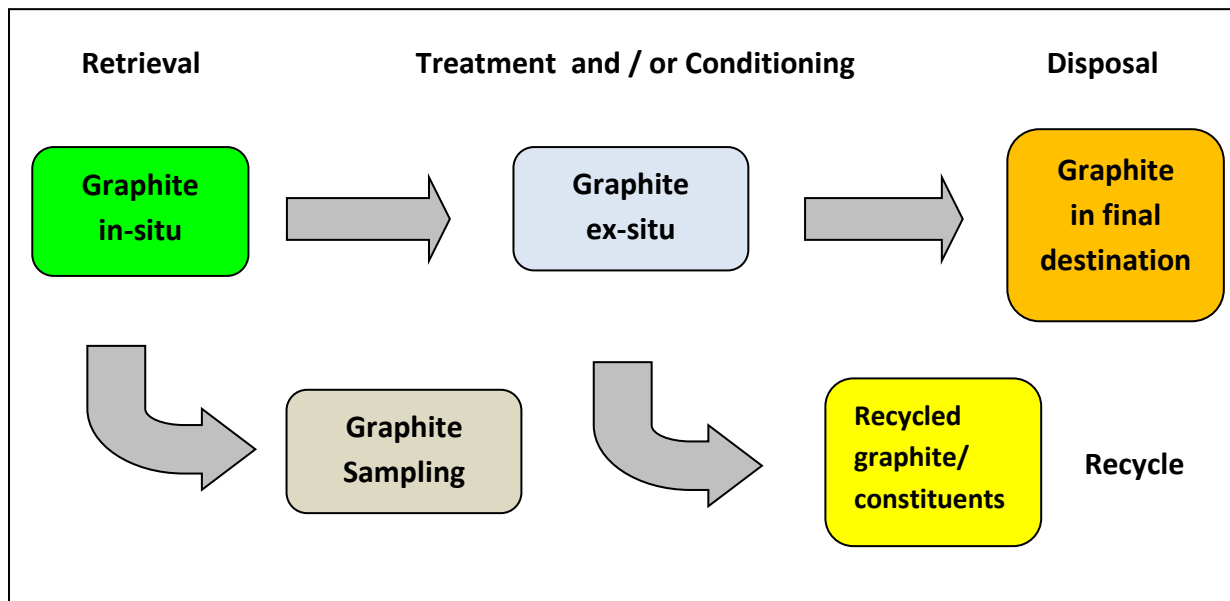


Figure 2: Graphite Waste Management System

The third stage has involved the development of a framework for the evaluation of the waste management options. This framework is a tool that will allow users to evaluate and compare the relative “sustainability” of different flowsheet options with regard to:

Environment and Safety

- Criterion 1: Environment and Public Safety
- Criterion 2: Worker Safety
- Criterion 3: Security

Economics

- Criterion 4: Economic Cost and Benefit
- Criterion 5: Technology Predictability

Social Issues

- Criterion 6: Stability of Employment
- Criterion 7: Burden on Future Generations
- Criterion 8: Social Acceptance

The fourth and final stage of the process will apply this approach to a range of individual case studies. This will involve the use of knowledge identified in the review phase and that resulting

from CARBOWASTE and other research and development activities, to calculate a range of flowsheet options. These options will then be evaluated using the criteria identified in a multi-criteria decision analysis (MCDA) framework. The aim of the MCDA is to inform decision making on i-graphite management routes.

4. Retrieval & Segregation

Key issues identified for the retrieval of i-graphite from the core are the access to the reactor, the condition of the graphite, the working environment (in-air, inert gas or underwater), operability and especially the preliminary or final waste route [4]. In most cases, retrieval of i-graphite was not sufficiently foreseen in the design of the former reactors, which often used thick-walled prestressed concrete pressure vessels without providing sufficient access to remove i-graphite blocks. In addition, i-graphite may be associated with other materials such as thermocouples, metallic spacers etc. These non-carbonaceous constituents also need to be segregated before entering into treatment or conditioning processes.

The properties of i-graphite are crucial to the retrieval and segregation not least because i-graphite may exist in a range of conditions e.g. in terms of morphology, weight loss, neutron dose, operational temperatures, coolant gas composition and factors related to position and utilisation within the reactor. These impacts upon access, contamination levels and tooling types. The Retrieval and Segregation study has taken account of these variables, the range of tooling necessary to cover any eventuality, the impact of particle size (bulk or particulate), the mix of materials encountered, the potential for dusts, the need for visibility and the need to for clear definition of the planning and design process leading to an optimum waste management solution.

Tooling selection is dependent on both the feasibility of handling the graphite and any associated access, reach and segregation activities, and also on the logistics of removing e.g. up to 4000 tonnes of i-graphite from a reactor, in an acceptable timescale. Any reasonable tooling including excavators, brushes and buckets, crushers and vacuum cleaners might be considered. Three tools used successfully on GLEEP and Windscale AGR included drill and tap, ball grabs and vacuum lifters.

The selection of i-graphite retrieval in-air, remotely or with manual intervention, leads to the potential of dust generation and release. Such operations require the selection of tools that keep dust formation to a minimum and tools and instrumentation that can be operated and maintained in the presence of graphite dust. There is also the need to collect the dust generated by i-graphite retrieval/tooling operation by the use of dust suppression systems and HEPA filters, which also then have to be correctly disposed. However dust samples can also provide additional characterisation data.

Underwater retrieval operations provide the benefits of radiological shielding, dust suppression, line of sight visibility and use of simple manually controlled close approach tools. An underwater approach is planned for at the French Bugey UNGG reactor [5]. Challenges to operations underwater include the requirement to consider water chemistry / corrosion issues, visibility and the retrieval of failed equipment. In this case a water treatment system is required with production of resins and filters.

Reactor configuration and structural considerations influence choice of environment even for different reactors of the same type. Also the choice may be dictated by the overall decommissioning process rather than solely an issue of i-graphite. But underwater operations may also reduce isotopic contamination, for example of ^{36}Cl by leaching processes.

Modelling has considered the lifting loads involved, potential to fracture the graphite blocks, the influence of weight loss and in some cases acceleration of the lift. The Finite Element Analysis of the tooling operation could form an integral part of the CARBOWASTE toolbox.

5. Characterisation of irradiated graphite

Characterisation within the CARBOWASTE Project is a “key issue” in the scheme of radioactive carbonaceous waste management and life-cycle. It is not a goal of the waste management itself but facilitates a better understanding of the nature of contaminants; contamination mechanisms that allows the prediction of isotopes by inventory modelling; the determination of decontamination factors; the selection of appropriate treatment methodologies and ultimately nuclide inventory determination for long term disposal.

Correlation and the scientific interpretation of the results from the innovative characterisation procedures for impurities location, structural analyses and modelling applied on virgin and irradiated graphite gives the validation and underlying principles for accurate data and a basis for making decisions in any step of the waste life-cycle: retrieval, treatment, conditioning, interim storage and final disposal. A novel example of the structural characterisation techniques currently being applied with the CARBOWASTE project is through the use of X-ray tomography. Manchester University has employed this technique to give 3D volume information of irradiated graphite microstructure, porosity size and shape distributions and to identify the location of high attenuation inclusions within the material which may be associated with contaminants and isotopes. A volume reconstruction of irradiated British Experimental Pile Zero reactor graphite is shown in Figure 3 and clearly shows the porosity distribution (blue) and inclusions of high attenuation (red).

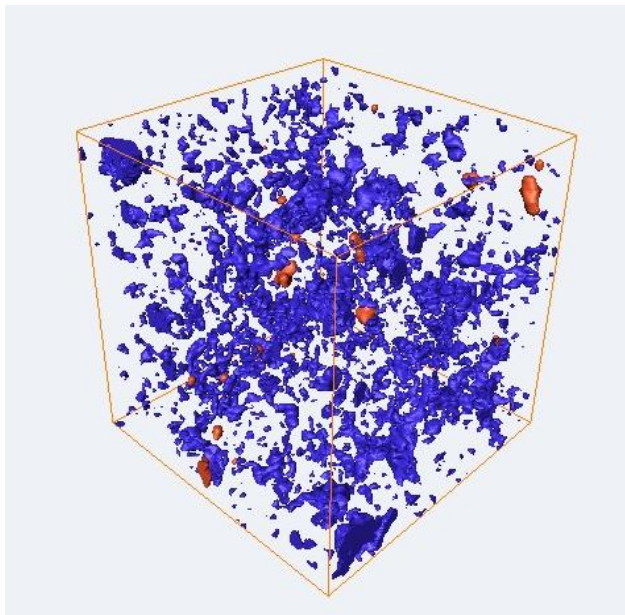


Figure 3: 3D volume reconstructions of 1 mm³ BEPO Graphite showing porosity

The laboratories involved in this characterisation have applied these methodologies over the main legacy waste in EU focusing not only in i-graphite from the most abundant reactors (Magnox, UNGG and MTR) but also i-graphite from RBMK or HTR reactors.

In order to upgrade, check and harmonise the radiochemical methodology a proficiency test (Collaborative mode) based on international standards has been carried out. The nuclides determined are ³H, ¹⁴C, ³⁶Cl, ⁶³Ni and ⁶⁰Co by ten Lab's for two samples of i-graphite powder

whose homogeneity is probed by ANOVA test, before distribution of samples. Preliminary results from the expert laboratories within the consortium have been consistent, which increases the confidence in the reliability of the analytical results and facilitates the validating and/or accreditation of test procedures.

Radiochemical analyses methodologies have been developed for this matrix and for the specific nuclides within this waste. In this field technology for sample preparation, dissolution of the matrix, accurate determination of gamma emitting nuclides, as well as beta-emitting ^3H , ^{14}C , ^{36}Cl , ^{63}Ni , ^{99}Tc , ^{129}I and alpha emitting nuclides has been developed and applied.

6. Treatment & Purification

The knowledge on the location and the chemical bond of contaminating radionuclides is a necessity for the development of methods for treatment and purification of i-graphite. Nuclear graphite is a technical product composed of filler and binder materials [6]. For filler, mainly coke (made from coal or petrol pitch) or natural graphite and additions of carbon black are used and, for binder, e.g. pitch or resins. These components are then heat-treated, impregnated and graphitized at temperatures beyond 3000°C , e.g. by the Acheson process. Carbon brick as also used in the German HTR (AVR, THTR) is only ‘baked’ to about 1200°C and can be considered as a nuclear carbon material with crystalline filler and highly amorphous binder regions. Figure 4 shows that the binder regions are the main place where impurities are located. The white dots indicate diverse impurities which have been detected by back-scattering electrons. These impurities mainly consist of oxides and carbides of aluminium, silicon and iron, but the easily neutron-activable elements cobalt and nickel are often affiliated to these main impurities as has been analysed by Secondary Ion Mass Spectroscopy (SIMS).

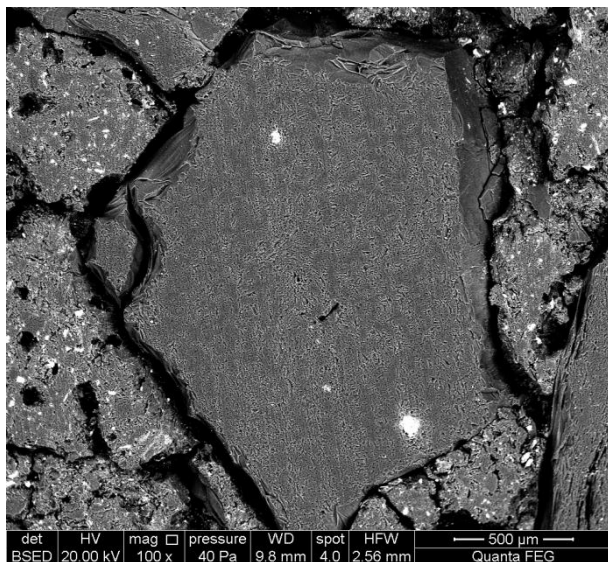


Figure 4: Scanning electron micrograph of carbon brick in back-scattering electron mode

It is evident, that non-carbon contaminants like ^3H , ^{36}Cl , ^{60}Co etc. can principally more easily be removed from the carbon matrix by specific separation processes due to their different chemical behaviour compared to carbon. But is it possible to remove ^{14}C from material that consists predominantly of ^{12}C and 1.07% of ^{13}C atoms; all of which have identical chemical features and are differentiated only by atomic weight?

The main routes for the generation of ^{14}C are via neutron activation of ^{13}C ($n, \gamma / 0.0014$ barn), ^{14}N ($n, p / 1.93$ barn) and ^{17}O ($n, \alpha / 0.257$ barn). Due to the fact that ^{17}O is only present in natural oxygen by 0.038%, ^{14}C generation via ^{17}O is much less than by ^{13}C or by ^{14}N , in most i-graphite cases. As the activation cross section for nitrogen is about 1,400 times larger than for ^{13}C , the same ^{14}C production rate is therefore already reached at a nitrogen concentration of about 8 ppm within the graphite. Much higher nitrogen concentrations (up to 40-300 ppm) have been measured in nuclear graphite, which has been exposed to air. However, the nitrogen content of graphite being irradiated under CO_2 as is the case for UNGG, MAGNOX and AGR can significantly differ from these results, due to nitrogen desorption under operational temperatures and coolant gas conditions. Reverse calculation methods based on the measured values of ^{14}C specific activity and their distribution within the core of shut-down reactors are therefore often applied to determine the sources of the ^{14}C generation [8].

It is known that graphite has a high affinity to nitrogen, which is chemisorbed on the surfaces of the graphite, up to a depth of about 50nm [9]. Under this background, it can be assumed that the ^{14}C atoms created by neutron activation of nitrogen will stay near to the location of the activated nitrogen atom, despite considerable recoil energy from the nuclear (n, p) reaction.

^{13}C is mainly bound in the graphite lattice and is part of other deposited carbon-particulate matter in the graphite. In case of the $^{13}\text{C}(n, \gamma)^{14}\text{C}$ reaction the recoil energy is high enough to dislocate the ^{14}C atom from its previous place in the lattice. It will either recombine with vacancies or stay or migrate as an interstitial between the graphene layers.

Experiments at Forschungszentrum Jülich [10] first revealed that ^{14}C was preferentially released when heating i-graphite in the range of 870-1300°C, in an inert atmosphere or in water steam.

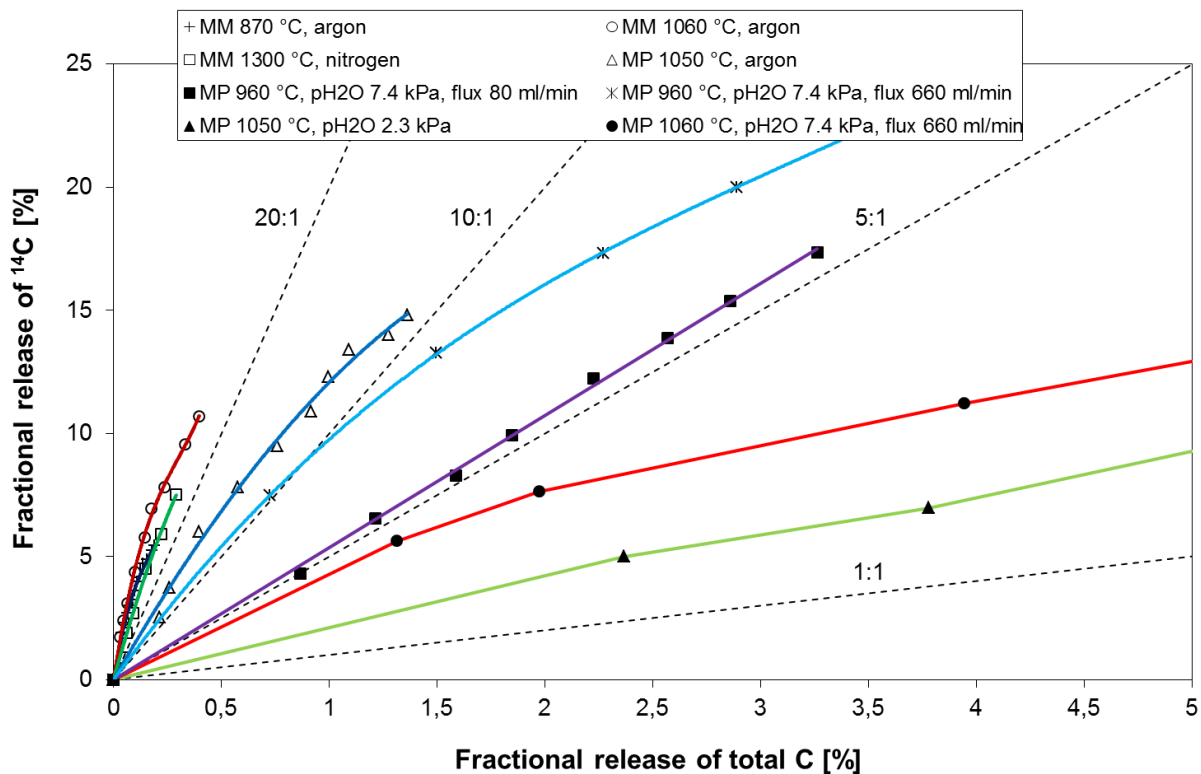


Figure 5: Fractional release of ^{14}C vs. total carbon releases of i-graphite from the FRJ-1 MTR (MERLIN) thermal column (MM-massive sample; MP-powdered sample)

The high ^{14}C release fractions when ‘roasting’ i-graphite under inert gas atmosphere can be explained by the fact that oxygen is also physi- and/or chemisorbed at the surfaces of the crystalline structures [11], in the direct ‘neighbourhood’ of the ^{14}C atoms. At higher temperatures, the oxygen reacts with all carbon atoms around including those ^{14}C isotopes formed by nitrogen activation until all available oxygen is exhausted. The graph in figure 5 also includes experiments with water vapour as oxidant. It can be seen that the ^{14}C release is rather sensitive to a variation of the process parameters and that there is still a lot of potential for improvements. A ^{14}C vs. total C release ratio of 1:5 can be seen as a lower limit for an industrial process development for ^{14}C removal. The ratios beyond 1:20 may even allow the development of ^{14}C extraction processes, e.g. for medical uses.

Recent studies at Forschungszentrum Jülich and at University of Manchester have shown that significant activities of the ^{14}C can also be removed through the use of thermal treatment with oxygen. The latest research carried out in Manchester has employed computerised x-ray tomography in conjunction with thermal treatment (*ex situ*) in order to decontaminate the graphite and identify the location of ^{14}C within the graphite matrix. Samples have been identified with laser markers to align in the CT scanner prior to thermal oxidation. Oxidation is then performed up to 1000°C in a 2% O_2/Ar environment. A bubbler system is connected to the catalytic furnace which traps ^{14}C and ^3H , which is then analysed using liquid scintillation counting. The irradiated graphite sample is then rescanned with X-ray tomography to determine weight loss and structural changes to the material.

However, it must be stated that such ^{14}C release processes already occur under operational conditions being mainly triggered by radiolytical and chemical corrosion of the graphite, in dependence of the specific coolant gas (e.g. air, CO_2 , helium), the impurities within the coolant gas (e.g. oxygen, nitrogen), the operational temperatures and the final neutron dose, which increasingly leads to an amorphisation of the graphite crystals. Therefore, it is difficult to compare different i-graphite features without taking their specific operational history into account. The final content of the ^{14}C is an equilibrium of the generation vs. release processes already during operation.

In case of shutdown UNGG reactors, reverse calculation methods have shown that the remaining ^{14}C is even less than ^{14}C generated by the ^{13}C contribution route. This clearly shows the strong competition of ^{14}C generation by neutron activation of ^{14}N and ^{13}C against the ^{14}C release in operational conditions due to chemical and radiolytic corrosion, at temperatures up to about 550°C.

Provisional interpretations of the ^{14}C releases indicate that a varying part of the ^{14}C is easier to remove than the remaining rest. This might be due to the fact that ^{14}C created by activation of ^{13}C will mainly be integrated into the lattice of graphite crystallites or as an interstitial atom between the graphene layers. For disposal purposes, it will be decisive that the mobile fraction of ^{14}C is preferentially removed or fixed, whereas the stable part will presumably not be released under disposal conditions.

Other problematic radioisotopes, ^3H and ^{36}Cl can also be removed by such treatment processes. The next figure shows the release of tritium during the ‘roasting’ under inert atmosphere. It can be seen that nearly all tritium can be removed at temperatures around 1300°C, at reasonable exposition times. It is assumed that the main effect is based on a pyrolysis of CH bonds, which degrade in relation to temperature.

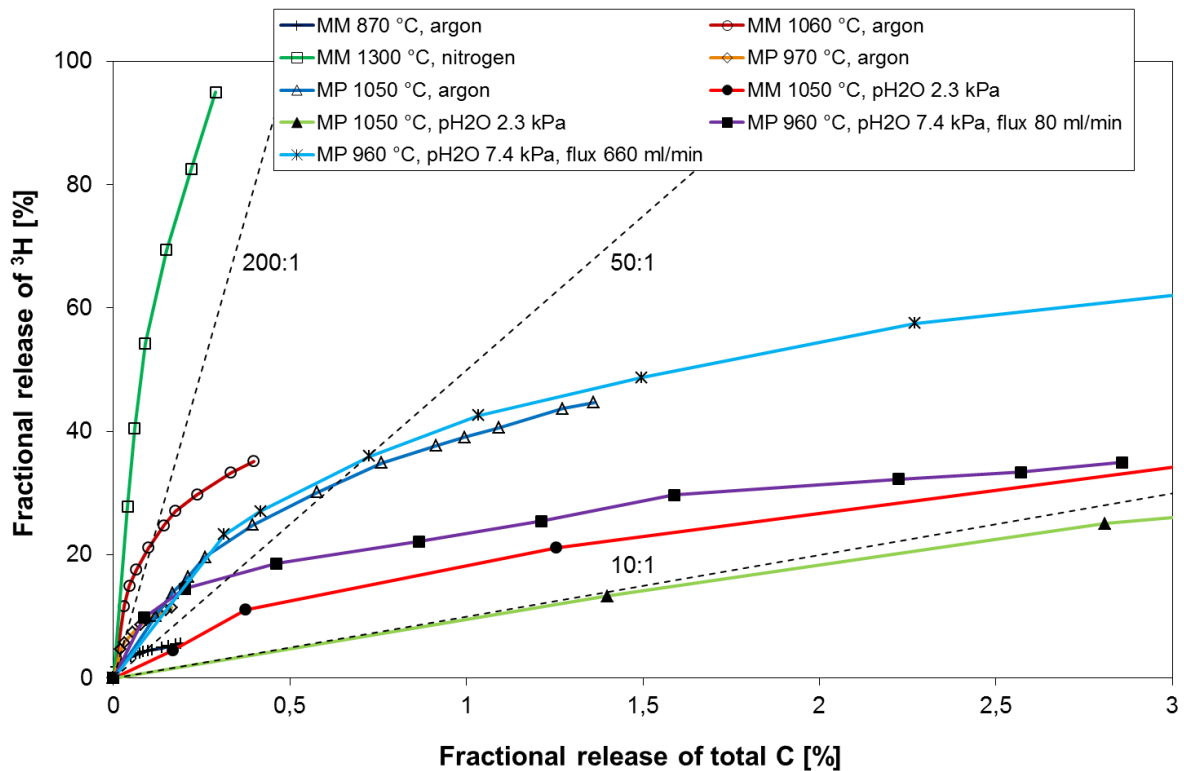


Figure 6: Fractional release of ^3H vs. total carbon releases of i-graphite from the FRJ-1 MTR (MERLIN) thermal column (MM-massive sample; MP-powdered sample)

Further treatment processes are investigated with several acidic leachants (HNO_3 , HCl , H_3PO_4 , H_2SO_4 , and mixtures of the aforementioned with Oxalic and Citric acids) in order to determine the decontamination factor e.g. for ^{60}Co , ^{94}Nb , ^{137}Cs , ^{154}Eu , $^{239,40}\text{Pu}$, ^{241}Am as well as for ^3H and ^{14}C . In addition, decontamination processes using diverse liquid detergents, molten salt, spark erosion, plasma, laser, blasting and electrochemical techniques are also under consideration. Another interesting study has been performed by the South African partners with microbiological treatment, which also shows certain selectivity for ^{14}C removal.

7. Reuse & New Products

Good environmental practice requires that the disposal of waste should be the last option selected and only after preferable alternatives have been considered, i.e.:

- minimisation of waste generation,
- reuse of materials in their current form or
- recycling the materials through appropriate processing to form new products.

The starting point in developing a viable strategy for the recycle/reuse of i-graphite is the establishment of a process, which takes i-graphite from its retrieved form and converts it into a suitable intermediate (e.g. carbon black) for its inclusion into products for use within the nuclear industry.

The treatment phase enables the release of the majority of the volatile ^{14}C from the graphite with minimal conversion of the graphite to the gas phase (<10%). This ^{14}C rich gas stream could then be utilised as a source of ^{14}C for use within the pharmaceutical industry. The ^{14}C would need to be purified and further enriched through the use of additional isotope separation techniques, e.g.,

Pressure Swing Absorption or Gas Centrifuge. The argument for extracting the ^{14}C from i-graphite is bolstered by the fact that the security of supply of ^{14}C for use in the pharmaceutical industry is presently becoming more uncertain.

The process of steam reforming is also suited for use with irradiated graphite together with a 'Roasting Process' as there is no inert carrier (nitrogen) involved in the process therefore the process can take place (more or less) in an enclosed system thereby ensuring the containment of radionuclides. The conversion of i-graphite into the gas phase results in the retention of the less labile radioisotopes such as ^{60}Co in the solid residue. This residue can then be packaged and grouted for long term storage. Additionally, with the liquefaction of carbon dioxide or reversal of the gasification process by the Sabatier or Bosch reactions there need not necessarily be any release of gas to atmosphere as a result of the process. In terms of maximising the recycle opportunity of the graphite, the reversal process (through the Sabatier or Bosch reactions) enables a convenient intermediate to be produced (carbon black) which can be incorporated (either partially or wholly) into the production of carbon based products for use within the nuclear industry.

Significant work is being undertaken in the identification and subsequent production of new carbon based products produced wholly or partially from recycled graphite for use within various facets of the nuclear industry [12]. These include the production of:

- Silicon Carbide (SiC) for use in disposal sites as a backfill or encapsulant,
- Absorbent material (e.g. Charcoal Filters) to remove nuclides from liquid / gaseous waste, and the manufacture of carbon nanotubes for use in waste disposal technology,
- New graphite for use in graphite moderators which consists (in part) of recycled graphite,
- Graphite Electrodes for use in waste vitrification.

The use of these recycled products aims to minimise the requirement for the use of similar virgin graphite products, thereby minimising waste generation. The production of the various carbon based artefacts is currently underway. The following evaluation phase will address the viability of using recycled graphite for new carbon/graphite products for use within the nuclear industry, through detailed assessment of the candidate products properties, characteristics and fitness for purpose.

7. Disposal

With regard to the disposal behaviour of i-graphite it has to be reminded that nuclear graphite is rather porous (typically ~20%) and that porosity even increases by irradiation and mass loss, during operation in the reactor. The radiation and radiolytic corrosion cause breakage of the C-C connections in the crystallites and/or the joints in the grains of graphite to form more hydrophilic C-H or C-O connections. Under this background, access of groundwater to the pore space within i-graphite has been studied e.g. at CEA for the release of radionuclides from graphite. The results show that small hydraulic gradients are sufficient for water infiltration into the pore space. Water saturation of a significant fraction of the open pore volume is rapid even at low pressures. Water access leads to almost instantaneous leaching e.g. of a significant part of the ^{36}Cl inventory of small sized graphite samples. Both diffusive and advective transport properties for radionuclide transport in graphite are analysed, as well as the influence of operating conditions during irradiation.

It is known that the reaction rate of graphite with water increases with an increase of the concentration of radiolytic water decomposition products such as H_2O_2 . This may lead to a release of the matrix bound fraction of the ^{14}C inventory. However, new calculations have shown that

after decay of ^{60}Co inventories, the expected dose rates will become so low that radiolytic processes will be insignificant for any additional ^{14}C release. Neither, pore water chemistry nor radionuclide release will be controlled by radiolytic graphite dissolution. This means that pore water chemistry will be similar to the composition of the groundwater, which might access the i-graphite disposal location in a geological formation.

The mechanisms, which govern the mobility of long-lived radionuclides like ^{14}C and ^{36}Cl under repository conditions prior to and after groundwater access are an important concern. XPS experiments carried out at the Institute of Nuclear Physics of Lyon on virgin and annealed samples show that around 30% chlorine is inorganic (chlorite or chlorate compounds) whereas around 70% is organic (aromatic C-Cl bonds). The release of inorganic compounds increases with temperature whereas the organic chlorine remains more stable. Only the latter is expected to resist to a certain degree under disposal conditions.

Radionuclides released from graphite may in principal be retained by engineered barrier materials surrounding the waste. However, first results show that e.g. ^{36}Cl retention on cementitious barriers is rather weak. Anorganic ^{14}C releases (e.g. $^{14}\text{CO}_2$) might well be kept in a concrete waste package whereas organic ^{14}C compounds (e.g. $^{14}\text{CH}_4$) might permeate through the concrete. Recent results indicate that only a small fraction of the ^{14}C inventory appears to be susceptible to mobilisation upon groundwater contact.

Disposal of i-graphite is being studied in many countries. Figure 7 shows an illustration for a specific i-graphite repository in a clay / marl sedimentary and low permeability layer, at a shallow depth ranging from 100 to 200 m. The layers should be at least 50 m thick and being located in a geologically stable zone over the next tens of thousands years and possess a low hydraulic gradient.

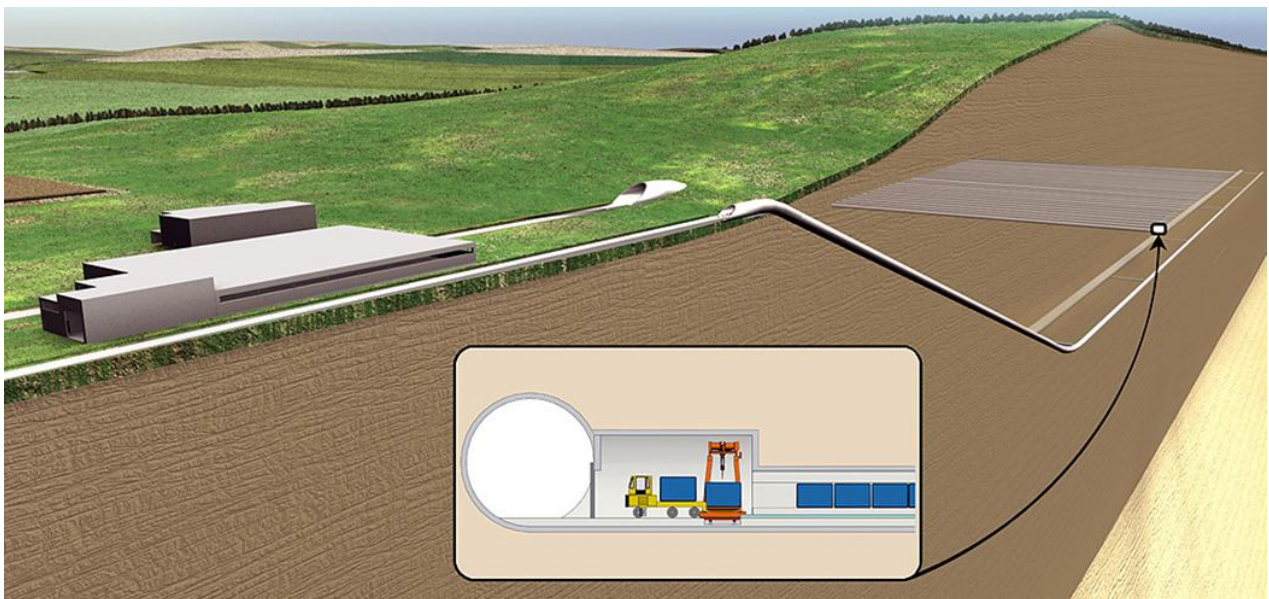


Figure 7: Concept of shallow disposal of i-graphite (courtesy of ANDRA)

Performance Assessment studies indicate that a cementitious backfill provides a strong chemical barrier for ^{14}C and that a clay backfill offers potential advantages for ^{36}Cl but the consequences of a reduced chemical barrier for ^{14}C need to be more fully understood. Increased ^{14}C flux to the geosphere in groundwater is unlikely to be significant, except where the geosphere is a poor barrier and ^{14}C does not substantially decay in the geosphere, e.g. due to the presence of fracture network to the surface. Potential hydro-fracturing of backfill also requires consideration. Coupled gas generation and multiphase flow calculations are required.

The disposal of i-graphite in the German KONRAD repository is investigated within the German CarboDISP project, which is complementary to the European CARBOWASTE project. The total ^{14}C activity being allowed for KONRAD is only $4 \cdot 10^{14}$ Bq. With an overall storage capacity of $303,000 \text{ m}^3$ this results in $1.32 \cdot 10^9 \text{ Bq/m}^3$, as an average. For the disposal of ^{14}C -waste in KONRAD, different limits result from safety analyses, which have to be considered. Most restrictive ^{14}C limits arise from safety issues for internal operation ($T \sim 50 \text{ }^\circ\text{C}$), classified by ^{14}C release from the waste container. If a maximum release of $\leq 1\%$ of the total ^{14}C inventory can be guaranteed, the limit is $1.8 \cdot 10^{10}$ Bq per container either individual or in average within a batch of containers. This means that about 22,000 waste-containers will be needed to accommodate the allowed total ^{14}C activity of $4 \cdot 10^{14}$ Bq. Taking as a basis a typical Type V KONRAD-Container volume of 10 m^3 , this number of containers corresponds to 70% of the total repository volume. If the 1% limit cannot be kept but ^{14}C releases may range up to 10%, then the maximum ^{14}C activity of a waste container must not exceed $1.8 \cdot 10^9$ Bq resulting in a ten times higher repository volume which exceeds the KONRAD capabilities. And if ^{14}C release cannot be specified the limit is even more restrictive being $1.8 \cdot 10^8$ Bq per container. Under this background, the CarboDISP project will focus on the ^{14}C release mechanisms under KONRAD operating and disposal conditions for German i-graphite waste including irradiated carbon brick, which contains a much higher ^{14}C contamination because of rather high nitrogen concentrations already present in the virgin material.

Summary

The management of irradiated graphite waste represents a considerable R&D challenge with regard to the retrieval, characterisation, treatment, reuse and final disposal of this specific material. There is a wide variety of graphite grades or other carbonaceous materials like carbon brick and of the conditions (e.g. temperature, gas compositions) under which they have been exposed to neutron irradiation. The impurities already manufactured into the nuclear graphite or added during operation finally determine the radio-contamination, after neutron activation.

It has been discovered that not only radioisotopes like ^3H , ^{36}Cl , ^{60}Co , ^{63}Ni , ^{94}Nb , ^{137}Cs , ^{154}Eu etc. can be removed with high efficiency from i-graphite by different purification processes but also a significant part of the radiocarbon despite the fact that ^{14}C has the identical chemical behaviour as the natural ^{12}C and ^{13}C isotopes.

This can be explained by the dominating generation of ^{14}C via the $^{14}\text{N} (n, p)^{14}\text{C}$ neutron activation process and by the phys- and/or chemisorption of nitrogen on the inner surfaces of the pore system of graphite. The ^{14}C atom in statu nascendi will preferentially adsorb on these surfaces, where ^{14}C is prone to corrosive attack either by the co-adsorbed oxygen or hydrogen or by corrosive gases added to i-graphite, at higher temperatures. Most of ^{14}C being produced by neutron activation of ^{13}C may be immobilized within the graphite lattice and will not significantly be released under disposal conditions.

Other purification processes like chemical decontamination, microbiological or electrochemical methods also provide promising first results. Reuse of i-graphite by manufacture of new products for nuclear use is a complementary option depending on the achievable decontamination factors of the purification processes. Certain radioisotopes like tritium and radiocarbon may be extracted in increased concentrations eventually allowing e.g. further use for pharmaceutical purposes.

Several options for underground i-graphite disposal are internationally under consideration. The leach behaviour of the porous i-graphite waste is investigated, in detail. In addition, waste packages and conditioning processes have to be adapted to this special type of long-lived radioactive waste.

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