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Synthesis of CARBOWASTE Work Package Findings

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Synthesis of CARBOWASTE Work Package Findings

Executive summary

The principal investigations in CARBOWASTE have ensured that the best-available and most environmentally acceptable technologies have been identified for characterisation, retrieval, treatment, reuse/recycling and disposal of irradiated graphite. This report presents the assimilation of key findings from CARBOWASTE into a coherent, integrated approach for the management of irradiated graphite wastes, such that readers may develop appropriate graphite management methods to meet their specific requirements.

Graphite is a complex inhomogeneous material and therefore generalisations about its behaviour during irradiation and its final condition are to be avoided. The source of material and its irradiation history are key factors which will determine the ultimate condition of the material, the quantity and location of radionuclides within the matrix, and the preferred options for its management.

Methods for the dismantlement of graphite cores include individual block removal and destructive, excavation-type processes. A period of in-reactor storage could reduce doses to operators by allowing the radioactive decay of shorter-lived radionuclides. Underwater retrieval could reduce dust and doses to operators but would generate aqueous waste that would require management. Segregation may be an option either during the retrieval process or during packaging after retrieval to separate different waste forms for treatment or disposal.

Partial decontamination by heat treatment and oxidation could offer credible options. Aqueous chemical treatment requires harsh environments which will necessitate careful process design but other chemical treatments such as steam reformation with off-gases incorporated in future carbon sequestration programmes could be more readily implemented. Intercalation processes using organic solvents may also be an option; however, decontamination by such processes generates secondary waste which will require management.

A range of waste package types and encapsulants are available for the retardation of radionuclide releases at disposal sites. The performance of waste packages has been investigated for a range of generic case geologies, but specific assessments will be necessary when final disposal sites have been selected. It may be possible to safely dispose of irradiated graphite wastes in the same vaults as other intermediate level wastes though there are benefits in separating large quantities of graphite.

The feasibility of recycle and reuse of irradiated graphite has been highlighted, although there is unlikely to be a sufficient market for significant quantities of irradiated graphite.

A process for the evaluation and comparison of graphite waste management options for irradiated graphite has been developed with multi-criteria decision analysis. Twenty four waste management options have been assessed to identify and test the process that can be utilised by the CARBOWASTE partner countries. Preferred options for different countries will vary depending upon specific national strategies, constraints and regulations.

The collaboration on harmonising methods for performing leaching experiments and pooling data has provided a more complete and rational understanding of radionuclide mobility. The project has created a European-wide collaboration on this specialist topic, which has now expanded to global cooperation through the International Atomic Energy Agency (IAEA). The work undertaken has achieved a better understanding of graphite waste management options through combining results and findings from different groups and has started to make a practical difference to national plans and actions in managing graphite. CARBOWASTE has been an excellent example of knowledge transfer to the “next generation”.

Table of Contents

1 Introduction 8
2 Position at the Start of the Project 9
2.1 Overview of Irradiated Graphite Management Internationally 11
2.1.1 France 11
2.1.2 Germany 11
2.1.3 Italy 12
2.1.4 Spain 12
2.1.5 Lithuania 12
2.1.6 Russia 13
2.1.7 UK 14
2.1.8 Other Member States 14
2.1.9 Asia 14
2.1.10 Japan 14
2.1.11 South Africa 15
2.1.12 USA 15
3 The Characteristics of I-graphite 16
3.1 Background 16
3.2 The Effects on Nuclear Graphite from Exposure in a Reactor Environment 17
3.3 Processes in Generating Contaminant Radionuclides 19
4 Graphite Management End Points 22
4.1 Stage End Points 23
4.2 Final End Points 25
5 Retrieval and Segregation Techniques 26
5.1 Factors Affecting Retrieval and Segregation Options 27
5.2 International Experience 27
5.3 Retrieval Options 28
5.4 Segregation Options 29
6 Treatment Processes 30
6.1 Introduction 30
6.2 Potential Treatment Processes 30
6.3 Experimentation 36
7 Disposal Assessments 38
7.1 Introduction 38
7.2 Radionuclide Releases under Repository Conditions 38
7.3 Repository Performance 40
8 Selection of Graphite Waste Management Options 42
9 Conclusions 48
10 References 50
11 Glossary 51

List of Tables

Table 1 List of twenty four options considered for assessment 42
Table 2 High level objectives for assessment of i-graphite management options 43

List of Figures

Figure 1 Schematic of i-graphite lifecycle 10
Figure 2 Schematic of vacancy and interstitial in graphite lattice 17
Figure 3 Schematic molecular cross-section of i-graphite showing typical distribution of contaminants 20
Figure 4 The Waste Management Hierarchy 22
Figure 5 CARBOWASTE End Points 23
Figure 6 Representation of the main steps in graphite exfoliation by organic solvent and ultrasound 34
Figure 7 Criteria Summary Diagram 44

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1 Introduction

CARBOWASTE Work Package 1 (WP1) "Integrated Waste Management Approach" has established an integrated waste management approach for the most significant sources of irradiated carbonaceous waste, and identified the most appropriate options for dealing with this kind of legacy waste. The outputs will enable comprehensive road maps to be developed based upon the most acceptable technical choices for each member state involved with the project. This work package comprises seven tasks and this report addresses one aspect of the final Task 1.7: Synthesis.

The specific task within Task 1.7: Synthesis addressed here is the assimilation of the key findings from all CARBOWASTE Work Packages into a coherent, integrated approach for the management of i-graphite wastes, such that readers may develop appropriate methodologies to meet their specific requirements. The Synthesis report has been compiled as a high level document; reference should be made to Collation of Data (Task 1.6), Work Package Summary Reports and within-Work Package references for more detailed information.

Within the CARBOWASTE project, five principal investigations have ensured that the best-available and most environmentally acceptable technologies were identified in the following areas:

- An integrated waste management approach being compatible with ecological, economic and socio-political requirements in Work Package 1, which includes a Multi-Criteria Decision Analysis (MCDA) assessment of a range of waste management options,

- Retrieval procedures which might affect the nature of the waste (e.g. wet or dry) as well as the radiological and core integrity effects of retrieval over a range of time horizons. Methodologies for separation of coated particles from the fuel matrix, in the special case of Very High Temperature Reactor (V/HTR) spent fuel (WP2),

- Characterising and then identifying suitable treatments for the carbonaceous wastes for removal of volatile and long-lived radioactive contamination (WP 3 & 4) associated with in-depth scientific investigations on microstructures and localisation of contamination including related analytical modelling,

- Elaboration of appropriate options for re-use and recycling of the graphitic materials, together with assessment of alternative options to bulk disposal in repositories (WP 5),

- Investigations and further research and analysis on the disposal behaviour of i-carbonaceous wastes (WP 6).

2 Position at the Start of the Project

The utilisation of nuclear graphite (i-graphite) in reactors as moderator, reflector or operational material leads to an accumulation of radioactivity by neutron activation both of constituent elements of the graphite and of impurities. Radionuclide inventories at reactor end-of-life depend on a range of factors, including impurity contents, irradiation history, reactor temperature and chemical environment. The principal long-lived radionuclide species present are C-14 and Cl-36, with shorter-lived species including H-3, Co-60 and small quantities of fission products and actinides. The particular radionuclides for consideration in any assessment of management options will be dependent on the regulations in each specific state. A fraction of these radionuclides is released during reactor operation due to thermal processes and, for some systems, oxidation (for example, carbon dioxide cooled graphite cores). I-graphite has a relatively low specific activity, yet due to the long half-lives of some of the activation products it remains radiotoxic for hundreds of thousands of years.

Irradiated and contaminated graphite from reactor moderators and reflectors or thermal columns, and other related carbonaceous materials, represent the greatest volume of waste materials from these reactors using these materials. Today about 250,000 t of i-graphite have been accumulated worldwide, ranging from countries with a suite of several graphite-moderated power reactors (e.g. UK/France) to prototypes, production and single experimental reactors. The large majority of this i-graphite exists either *in-situ* within reactors or in vault/silo storage.

The first stage in any approach to graphite management is a period during which the graphite remains, *in-situ*, within the reactor core, also known as a “safe enclosure” period (IAEA, 2006). This period prior to graphite removal can vary considerably, and may be up to several decades. The primary benefit of delaying retrieval is from the reduction of the radioactive inventory via the radioactive decay of the shorter-lived radioisotopes, such as Co-60, which may reduce the hazards associated with handling. Some consideration has been given to *in-situ* decommissioning, whereby the reactor is entombed within an immobilising material, such as concrete. In this case, graphite would not be retrieved from the reactor.

In approaches that consider i-graphite retrieval, graphite may be stored, either on the same site as the reactor, or in a centralised store prior to, or following, any treatment or processing options that might be employed. Such storage periods may be required at various stages of an i-graphite management approach, prior to any treatment/recycle/encapsulation/disposal facilities becoming available.

Apart from periods of storage (either *in-situ* or *ex-situ*), conventional graphite management is currently limited to two general approaches, the selection of which is largely due to the level and nature of the radioactivity associated with the graphite, as well as the volume of the specific graphite waste stream. The primary approach involves encapsulation of the graphite waste for long term storage / disposal within a suitable repository environment, which, for many countries, is currently anticipated to be required for the large majority of i-graphite.

The second approach, which is likely to only be suitable for lower activity graphite from, for example test reactors, involves incineration with either discharge of the resultant gas to atmosphere, or a process of carbon capture.

Both of the above approaches have inherent issues associated with them, such as radioactive discharges to the environment, conventional environmental impacts, capital costs and burden on future generations. A number of alternative, emerging graphite management approaches, such as decontamination, have been examined as part of CARBOWASTE.

To date, practical experience has been gained from the decommissioning of four reactors containing i-graphite:

- The Graphite Low Energy Experimental Pile (GLEEP) at Harwell, UK;
- The Windscale Advanced Gas-cooled Reactor (WAGR) at Sellafield, UK;
- The Fort St Vrain power plant in Colorado, United States; and
- The Brookhaven graphite research reactor at Long Island, United States.

Figure 1 provides a schematic diagram of an example i-graphite lifecycle, showing the principal mechanisms for the formation and release of radioactive carbon and chlorine species through all the stages from graphite manufacture to final disposal.

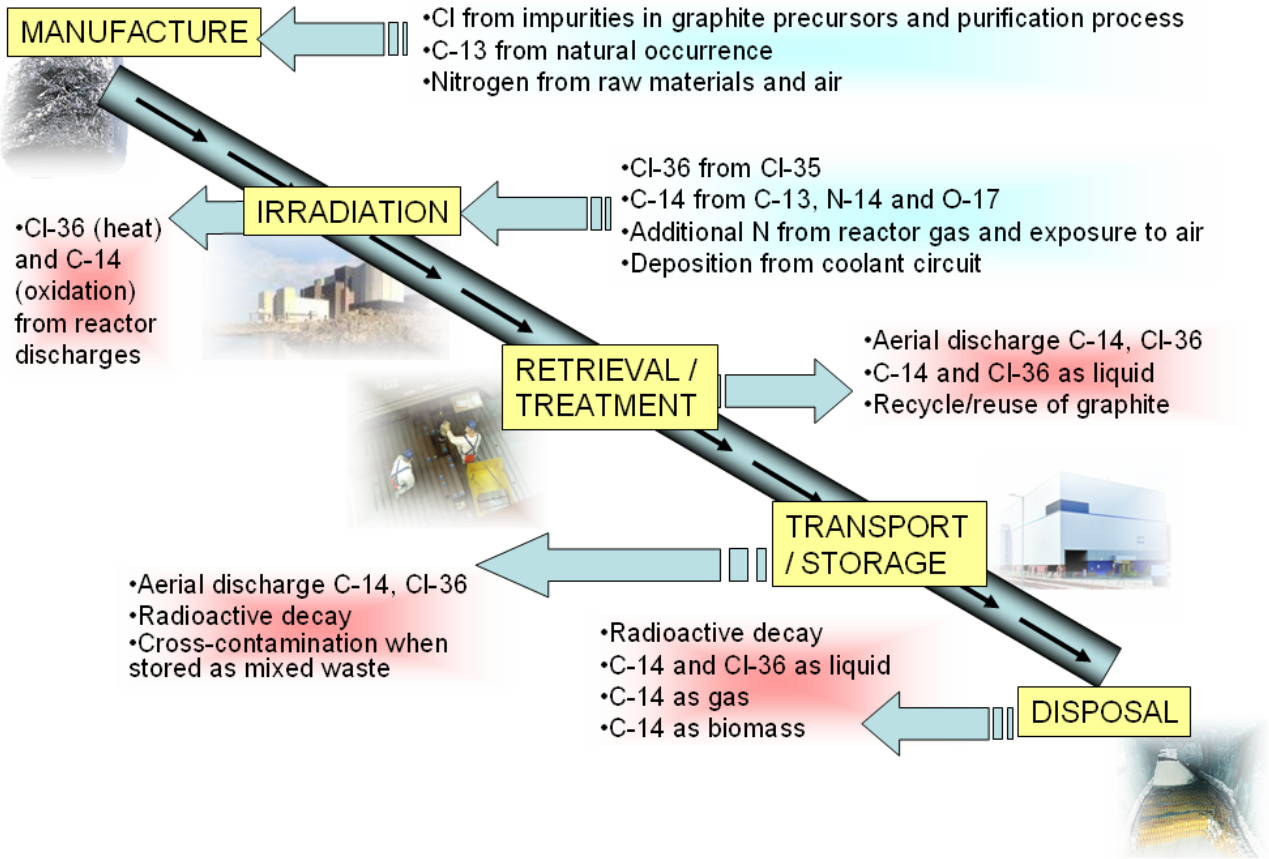

Figure 1 Schematic of i-graphite lifecycle

2.1 Overview of Irradiated Graphite Management Internationally

The following provides an overview of the situation as it was in 2009 (shortly after the start of the CARBOWASTE project) regarding irradiated graphite and its management internationally (both project member states and other countries). Present day updates to positions are provided in italics, where information is available.

2.1.1 France

In France, about 23,000 t of irradiated graphite is stored, originating mainly from nine UNGG reactors (Gas Cooled Reactors). Most of the irradiated graphite is present in shut down reactors except for small quantities of graphite sleeves temporarily stored in silos. EDF and CEA, who were the operators of the nine UNGG reactors from the 1960s to the 1990s, are the main producers of irradiated graphite in France. For all nine UNGG reactors, the IAEA level 2 decommissioning status had been achieved.

In 2001, EDF took the decision to achieve IAEA level 3 decommissioning status before 2025 for the six EDF UNGG reactors, including three other shut down reactors without irradiated graphite. The UNGG Bugey 1 reactor was intended to be the first UNGG reactor to be dismantled. The decision was taken by EDF that the dismantling works would be done underwater, mainly because the shielding afforded by the water would enable a more “hands on” approach to be adopted rather than a fully remote operation. It is considered that it allows a greater flexibility to respond to unforeseen technical problems during dismantling. ***Filling with water will begin in 2017 or 2018, with the first graphite bricks planned to be retrieved from Bugey 1 in 2025.***

French irradiated graphite waste from UNGG reactors is considered as Low-Level activity waste but because of the presence of small amounts of the long-lived C-14 and Cl-36 radionuclides and significant amounts of H-3, their disposal at the existing Centre de l’Aube surface repository site for Low-Level and Short-Lived waste is not acceptable. A new repository site for irradiated graphite is to be commissioned.

The preliminary irradiated graphite radiological inventory has been assessed from the highest measured values for each radionuclide among the numerous samples that have been analysed. This method led to an overestimated radioactive inventory used for preliminary studies on disposal. A new method based on data assimilation and activation calculation was being developed by EDF. Its objective was to provide a more realistic inventory for safety studies on disposal that is able to explain the variation in radionuclide measurements that have been observed depending on the sample localisation.

2.1.2 Germany

Two helium-cooled high temperature pebble bed reactors have been built and operated in Germany. The AVR, a 15 MWe experimental reactor at Jülich was shut down in 1988 after 21 years of operation. The 300 MWe prototype Thorium High Temperature Reactor (THTR) was operated from 1985 until 1989 in Hamm-Uentrop. Both reactors were permanently shut down and were at different stages of decommissioning. ***The AVR reactor has undergone a process of temporary concrete entombment, followed by transport of the whole pressure vessel and its internals to a storage facility, with the long term plan of dismantlement and ex-situ decommissioning.***

The moderator graphite was an integral part of the spherical fuel elements of the AVR and THTR and has to be managed separately. Until the end of the 1970s, a closed fuel cycle concept with reprocessing of the thorium-based spent fuel, similar to the US, was developed in Germany. This included the mechanical disintegration of the fuel elements, incineration of the moderator graphite, and recovery of the fissile material from the fission products by extraction. In early 1980, the Government decided to stop Research & Development on recovery, mainly due to economic reasons. Since then, the back-end option for the spent fuel has been based upon direct disposal in a deep repository without recovery, thus using the special safety features of the fuel elements, i.e. the coated particle fuel stabilised in a graphite matrix, which is extremely resistant to radionuclide migration during storage and geological disposal.

The spent fuel elements were removed from both reactors and are stored in CASTOR-type transport/storage casks in dry interim storage facilities on-site (at Jülich for the AVR) and at Ahaus (for the THTR) for up to 30 years, until a deep geological repository is available.

Graphite and low-purity carbon were used in both reactors for reflector, thermal insulation and shielding purposes. There is also a limited amount of graphite (reflectors, thermal columns) with low activation from water-moderated research and material test reactors in Germany. A 10 MWe research reactor (Merlin type) with two thermal columns was operated at Jülich for 23 years and decommissioned to greenfield status. A 23 MWe heavy-water material test reactor (DIDO) was operated at Jülich for 45 years and shut down in 2008.

2.1.3 Italy

Although Italy has constructed four commercial reactors, only one (Latina) was graphite moderated. All of these commercial reactors are shut down. It is estimated that about 2,100 t of i-graphite will arise from the decommissioning of the Magnox-type Latina reactor. The radionuclide composition of the irradiated graphite is based on predictions that are similar to the UK's Magnox reactor values. Ten experimental/test reactors have been constructed with about half of these still in operation. The quantity of graphite in these reactors is unknown.

2.1.4 Spain

There were two graphite-moderated reactors in Spain, Vandellos 1, a 460 MWe commercial reactor and a material test reactor, JEN-1. The isotopic composition of the graphite sleeves from Vandellos 1 and the thermal shielding of JEN-1 have been reported. The C-14 content of the sleeves is significantly higher than the shield material. This trend is true for all other isotopes measured.

In addition to the irradiated-graphite in these two reactors (2,700 t) more than 1,000 t resided in three silos. ***Retrieval of i-graphite from the Vandellos silos has been completed.***

2.1.5 Lithuania

Ignalina Nuclear Power Plant (INPP) was Lithuania's only nuclear power plant. Two RBMK-1500 type Soviet designed reactors (water-cooled graphite-moderated channel type reactors) were installed at INPP.

In accordance with National Energy Strategy adopted by the Lithuanian Parliament, the first unit of INPP was shut down at the end of 2004 and the second unit in 2009. The Lithuanian Government approved the immediate dismantling concept for the decommissioning of the first power unit of INPP. The INPP graphite waste consisted of shattered graphite sleeves originating from spent fuel channels and control and protection system (CPS) channels, of graphite bricks and sleeves resulting from decommissioning. Estimated quantities of graphite waste to be dealt with were 55 t of operational waste and 3,788 t of decommissioning waste (graphite bricks and sleeves for the two units).

According to the INPP Final Decommissioning Plan, graphite waste will be stored in non-shielded containers regardless of its radionuclide composition.

The Lithuanian waste management agency (RATA) interim waste acceptance criteria show that the INPP graphite waste does not meet the criteria for near-surface disposal due to the C-14 inventory. Disposal of graphite waste should therefore occur, after further treatment/conditioning, in a repository suitable for long-lived waste, in cavities at an intermediate depth or in a deep geological repository.

2.1.6 Russia

In total fifteen water-cooled graphite-moderated power reactors (eleven RBMK-1000 and four EGP-6 reactors) have operated in Russia. Three first-generation water-cooled graphite-moderated reactors (AM reactor in Obninsk and two AMB reactors at Beloyarsk NPP) are permanently shut down.

It was assumed that the best strategy for handling graphite during decommissioning of the power-generating units of a nuclear power plant with uranium-graphite reactors is localisation and long-term storage of the graphite components together with the reactor in a concrete shaft at the plant site under surveillance. In 1998 a unique experiment on withdrawing of the graphite column from reactor RBMK-1000 of Leningrad NPP Unit 3 was performed. The graphite column (all 14 graphite bricks) was withdrawn from cells 12-36 of RBMK-1000 of Leningrad NPP Unit 3, after 18 years of reactor operation, for long scale investigation of graphite brick behaviour and assessment of methods for graphite core dismantling.

Thirteen high-capacity weapons-grade plutonium production reactors were in operation in Russia. The decommissioning concept for these reactors was developed in the mid 1990s, comprising the dismantling of low-activity structures, sealing of all reactor outlets, and filling of all reactor spaces with special compounds of concrete and bentonite. All these arrangements were designed to ensure multi-level protection with a number of safety barriers between the reactor and the environment. The reactor shaft was intended to be transformed into the permanent radwaste repository. Since then, the approach has been redefined to one of monitored safe storage.

Due to the focus on *in-situ* storage and/or decommissioning, there has been little development of technologies for the treatment of i-graphite in Russia. However, work has been undertaken to develop molten salt technology for the treatment of graphite that has undergone spent fuel contamination, converting it into a stable vitrified product in a single process operation.

2.1.7 UK

Graphite has been used extensively in the UK nuclear programme, in eight experimental/production/prototype reactors, eleven Magnox stations and seven AGR stations. A production reactor at Windscale suffered a fire in 1957, after which it, and its twin reactor, were shut down. The fire-damaged reactor still contains a significant quantity of i-graphite. ***Of the base-load reactors, one Magnox reactor (at Wylfa) and all the AGRs remain in operation, whilst the remaining Magnox stations are shut down awaiting decommissioning, in line with the UK "safestore" approach, which is expected to include a 70 to 80 year delay period prior to i-graphite retrieval.***

The UK irradiated graphite inventory is large, with a total of over 80,000 m^3 forecast to arise. It is planned that most of this graphite will eventually be routed to geological disposal.

The UK has practical experience of decommissioning graphite reactors gained from work on GLEEP at Harwell and the prototype AGR at Windscale (WAGR). In both cases, graphite was retrieved from the cores in air, although the higher radiation associated with WAGR required a higher degree of remote handling.

A significant quantity of i-graphite exists in vaults and silos, mixed with other waste types.

2.1.8 Other Member States

Although Belgium, the Netherlands, Romania and Switzerland have invested in nuclear reactor development, the likely combined arisings of irradiated graphite represents a small proportion of the EU total quantity. Consequently, information regarding graphite characteristics is sparse but may be expanded when decisions are taken to decommission the three/four demonstration reactors, some of which are still in operation.

The criteria for retrieval, possible treatment and disposal that these Member States will need to consider could have many similarities with considerations that will be examined by other Member States that have invested in graphite-moderated reactors.

2.1.9 Asia

China currently has numerous research reactors that may contain small amounts of graphite, and HTR-10 which contains about 65 t. As HTR-PM reactors come on line, the graphite waste inventory will increase significantly. The first pair of HTR-PM reactors will contain about 1000 t of graphite. North Korea has operated a 5 MWe research reactor at Yongbyon. No reference to the volume of graphite at this plant has been found.

2.1.10 Japan

Japan is in the process of decommissioning the Tokai-1 power station, a graphite-moderated reactor of Magnox design. This was Japan's first commercial nuclear power plant and ceased generating at the end of March 1998, after 32 years of operation. Tokai-1 is the first commercial nuclear power plant to transfer to the decommissioning stage in Japan. The project therefore has important roles for demonstrating the safe and economical decommissioning of a nuclear power plant and

establishing key technologies for future reactor decommissioning in Japan. Graphite represents a significant element in relation to the challenge of the Tokai-1 decommissioning project.

In addition to the Tokai-1 plant, a High Temperature Test Reactor (HTTR) has been commissioned more recently.
There are two main strategies under consideration as a final disposition for graphite, although neither of these has been selected as the preferred option:

- Packaging for direct disposal in a geological facility; and
- Incineration with subsequent treatment of off-gas to reduce levels of the long-lived radionuclide C-14.

2.1.11 South Africa

European nations possess various quantities of irradiated graphite from reactors past and present. As such, the primary interest for these countries is strategies for managing the material they have or expect in the near term. South Africa offers a different perspective regarding graphite in Pebble Bed Modular Reactor (PBMR) fuel and structural materials with respect to its post-irradiation management. ***Since the abandonment of the PBMR concept, South Africa has continued to share knowledge about its graphite waste minimisation research with the CARBOWASTE project, in particular, offering results of experiments performed to prove the concept of microbial treatment of irradiated graphite to remove radionuclides, especially C-14.***

2.1.12 USA

There are 34 nuclear reactors listed in the Department of Energy (DOE) inventory as having graphite incorporated into the design. However, only twelve of these reactors contain (or contained) significant volumes of graphite: the Hanford production reactors, the Brookhaven Graphite Research Reactor, the Peach Bottom experimental high temperature gas reactor and the decommissioned Fort St Vrain high-temperature gas-cooled reactor (for which the graphite could be removed as part of a designed operational process). The amount of irradiated graphite in the US is estimated to be approximately 15,000 t, based upon volumes of material from these sites.

There are two approaches to decommissioning in the US, depending upon whether the nuclear plant is within the commercial sector licensed by the Nuclear Regulatory Commission (NRC) or is managed by the US DOE. In the case of plants under the jurisdiction of the NRC, three methods for decommissioning are available: DECON (immediate dismantlement), SAFSTOR (a facility maintained to allow decay of radioactivity, later followed by dismantlement) and ENTOMB (entombment and monitoring). The DOE approach covers transition, deactivation, surveillance and maintenance and decommissioning.

Decommissioning of US nuclear reactors containing graphite includes the dismantlement of the Fort St Vrain plant under DECON, the dismantlement of the SR 305-M Test Pile at Hanford (DOE jurisdiction) and the decommissioning and burial on site of the CP-2 (formerly Chicago Pile 1 and under DOE jurisdiction). ***The graphite from the decommissioned Fort St Vrain and Brookhaven reactors is now in long-term storage on DOE sites, which is regarded as final disposal. At present, the US has no plans for the treatment of irradiated graphite.***

3 The Characteristics of I-graphite

3.1 Background

The behaviour of nuclear graphite during irradiation and its final condition as a waste material will depend upon a number of factors:

- Nuclear graphites have been manufactured from a range of raw materials using different manufacturing processes leading to differing physical, mechanical, thermal and chemical properties. This includes differing impurity levels that may be radionuclide precursors.
- Compared with its manufactured state, irradiated graphite may undergo significant changes to its physical, mechanical and thermal properties.
- Nuclear graphites have been selected for a range of different roles in a reactor – moderator/shield/reflector/fuel assembly, each having different exposure environments.
- The characteristics of irradiated graphitic components having the same role in a reactor can vary depending upon their position in the reactor.

Given the above, there is no generic radionuclide inventory of i-graphite. The inventory is dependent on the source of the graphite and its reactor environment. Equally, there are variabilities and uncertainties depending on the method chosen for determining radionuclide inventories which must be taken into account when developing waste management options. Whilst radionuclide inventories can be developed using activation modelling, there needs to be a certain amount of direct measurement of representative material. It is known that there are two principal routes for the formation of C-14: via N-14 and C-13, either of which may dominate, depending on reactor conditions.

Knowledge of radionuclide precursors will inform the potential methods for treatment and of release mechanisms in a repository. Precursor species may be present in different parts of the graphite matrix (e.g. on the surface, in pore volumes and within the graphite lattice) and therefore have a significant influence on the degree of heterogeneity of radionuclide distribution in i-graphite. Its location will determine its mobility; its distribution may provide potential for segregation.

The CARBOWASTE project has sought to improve international consensus on the characteristics of i-graphite through an extensive programme of experimentation and modelling. This work has included:

- Validating analytical methods for inventory determination in irradiated graphite by a proficiency test applied to real graphite waste;
- Determining the type and location of impurities and radioactive isotopes in un-irradiated and irradiated nuclear graphite within the selected grades and sources;
- Determining the mechanism by which impurities / radioactive isotopes may be removed from nuclear graphite by various treatments;
- Determining the stability of radioactive isotopes in nuclear graphite before and after treatment;

- Undertaking inter-comparisons on irradiated and non-irradiated graphite samples from a wide range of sources.

3.2 The Effects on Nuclear Graphite from Exposure in a Reactor Environment

Nuclear graphite is a non-homogenous, composite material typically manufactured from petroleum or coal-tar derived cokes with a pitch binder, and formed in a manner such as to make it isotropic, or near-isotropic. It is noted that the processes occurring when such non-homogenous nuclear graphites are irradiated within a reactor are complex. The following therefore represents only a simplified description of the general phenomena and key processes.

The irradiation of graphite within a reactor can potentially lead to three types of change in the material. In addition to affecting operation of the plant, these changes may also subsequently impact upon dismantling, handling of the material during decommissioning, treatment and disposal. The processes associated with these types of changes are:

- damage caused by fast neutron irradiation leading to physical, mechanical and thermal property changes;
- chemical changes produced by the irradiation leading to physical, mechanical and thermal property changes; and
- activation of impurities and transported materials deposited in the graphite pores leading to induced radioactivity.

When a fast neutron collides with a carbon nucleus, while passing through nuclear graphite, atoms are knocked out of their lattice positions and interjected into the immediate surroundings. Two simple types of lattice point defects are produced in equal numbers: interstitials, which are the displaced atoms themselves, and vacancies which are the atomic holes/gaps left behind (Figure 2).

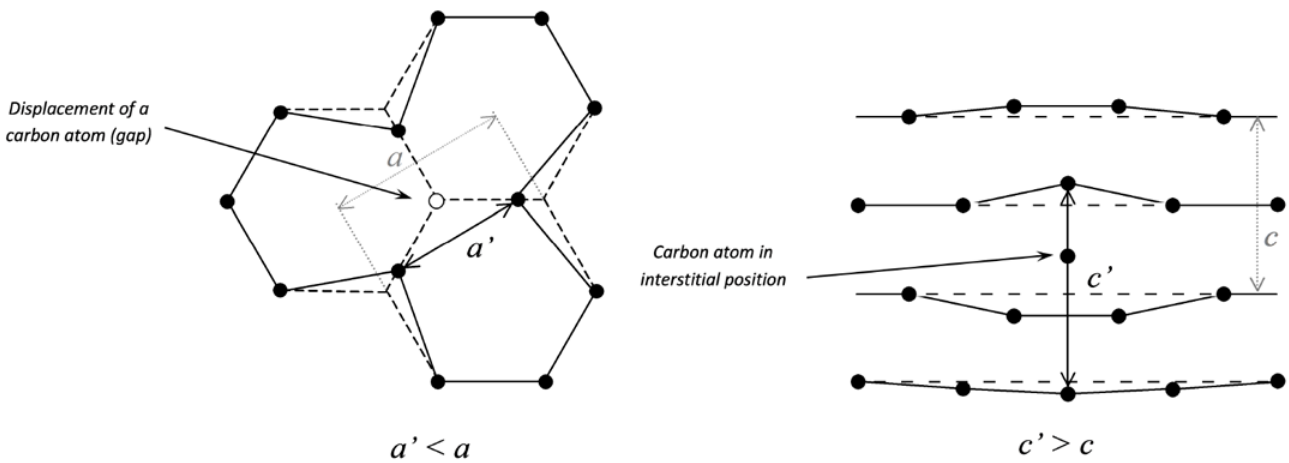

Figure 2 Schematic of vacancy and interstitial in graphite lattice

In practice, however, the damage is more complicated than this because these point defects are created as, or quickly regroup themselves into, clusters of various sizes and forms. The net result within an individual crystallite is an expansion in the 'c' direction and a contraction in the

perpendicular 'a' directions. In the polycrystalline material, crystallite directions are randomised or at least partially randomised and this, together with the presence of void spaces (porosity), means that dimensional change of the polycrystalline material is much less than the dimensional change of individual crystallites. The net behaviour is complex, especially in non-isotropic materials, and can have a profound effect on properties through changes in porosity and interconnectivity. In addition, the pinning of basal planes by interstitials and clusters of interstitials in the crystallites modifies the shear behaviour between basal planes, thereby affecting the mechanical properties of the bulk material. Crystal defects will affect electrical and thermal conductivity. Property changes due to irradiation damage could affect dismantling options. In particular, dimensional change will lead to the distortion of components which could affect disassembly.

One further significant effect arising from irradiation damage is the accumulation of Wigner energy by the displacement of carbon atoms into higher energy state interstitial positions. The quantity of accumulated stored energy is a function of fast neutron flux, irradiation temperature and time. The accumulation of irradiation damage will be offset by thermal annealing. The higher the irradiation temperature, the lower will be the amount of stored energy. At all irradiation conditions, a saturation point may be achieved in terms of the total amount of stored energy for long periods of irradiation. The stored energy is capable of release if the material is heated above its irradiation temperature. An increase of 50K above the irradiation temperature is sufficient to achieve a significant energy release rate although temperatures in excess of 2000°C are required to purge all Wigner energy. Energy release is considered only to be of concern where it occurs at a sufficient rate that self-accelerating energy releases become possible.

In carbon dioxide environments, radiolytic oxidation will occur when the gas reacts with ionising radiation to produce an oxidising species. These reactive oxidising species absorb on a graphite surface, and lead to graphite oxidation associated with a release of adsorbed radioisotopes. The rate of radiolytic oxidation of the graphite depends on the gamma energy absorbed by the carbon dioxide within the pores of the graphite. Graphite exhibits various degrees of radiolytic oxidation, for example in highest flux region of a Magnox reactor core weight losses from such oxidation can be up to ~40% from the virgin state. Oxidation will lead to degradation of the graphite properties, including hardness, strength and thermal conductivity.

Processes for generating radionuclides in graphite are discussed in section 3.3 below. Such pathways may arise via impurities in the manufactured graphite and by transport of radionuclides or their precursors to the graphite from other regions of the reactor system. The determination of radionuclide inventories in irradiated graphite relies on a combination of sampling with radionuclide analysis and activation modelling (requiring some knowledge of precursor impurity levels).

The processes described above are generic and, for specific nuclear graphite, consideration of its physical properties and of its behaviour during irradiation must be taken into account when determining its final condition as a waste material. Nuclear graphites will have been manufactured from a range of raw materials using different manufacturing processes leading to differing physical, mechanical, thermal and chemical properties. This includes differing impurity levels that may be radionuclide precursors. Nuclear graphites will have been selected for a range of different roles in a reactor – moderator/shield/reflector/fuel assembly, each potentially having different as-manufactured properties and exposure environments. Therefore there is no generic graphite dataset that can be assumed. Furthermore, compared with its manufactured state, irradiated graphite may

undergo significant changes to its physical, mechanical and thermal properties and these changes will vary depending upon reactor type and operating history. Finally, the characteristics of irradiated graphitic components having the same role in a reactor can vary depending upon their position in the reactor. In particular, the radionuclide inventory of any sample of irradiated graphite should be understood prior to treatment to enable the most appropriate technology to be selected. The treatment of irradiated graphite may offer the opportunity to separate radionuclides which pose problems (such as C-14) from the less problematic radionuclides. The importance of such considerations will vary depending upon the selected waste management option and, in the process of selection, the level of characterisation of the irradiated graphite will need to be assessed and justified.

3.3 Processes in Generating Contaminant Radionuclides

Mechanisms

There are several mechanisms for the production of key radionuclides in i-graphite, and these vary according to the physical characteristics of the graphite and the environmental conditions in the reactor. C-14 may be mainly generated by the reaction N-14(n,p)C-14. Nitrogen is incorporated into the graphite matrix because graphite manufacture is typically done in a nitrogen-rich atmosphere. Nitrogen may also be present in varying concentrations in the coolant gas of an operating reactor and may therefore be deposited on the graphite surface. A second, equally significant pathway is via C-13(n,γ)C-14. Production from either O-16 via O-16(n,γ)O-17(n,α)C-14 or directly from O-17 is a minor, but non-trivial, route in coolants of operating reactors containing oxygen isotopes.

The use of either chlorine gas or freons in the purification process during graphite manufacture to remove certain metallic impurities as their volatile chlorides, can lead to residual Cl-35 contamination in addition to chlorine already present as impurity in the filler and binder materials. Cl-36, arising from activation of residual chlorine used in such purification processes represents another significant contaminant of irradiated waste graphite. This isotope is important as it is long-lived and poorly retarded by geological barriers.

Another significant radionuclide contaminant in i-graphite is tritium (H-3). H-3, which has a half life of 12.3 years, is mainly produced from the neutron activation reaction Li-6 (n, α). Very small amounts of H-3 probably occur also from He-3 (n, p) and H-2 (n, γ). H-3 is a low energy beta emitter, leading to detection issues. H-3 is significant when early management of i-graphite is considered. Where retrieval and treatment is delayed for a period of several decades following reactor shut-down, H-3 activity will largely have decayed away to low levels.

In addition to the activated radionuclides, graphite may also be contaminated with radionuclides arising within the reactor circuit, from either fuel element failure or activation products circulated in the coolant. Radionuclides from corrosion products and lesser impurities may include: Ca-41, Fe-55, Ni-59, Ni-63, Co-60, Ag-110m, and Cd-109. Further, quantities of fission products (Sr-90, Zr-93, Tc-99, Pd-107, Cd-113m, Sn-121m, I-129, Ba-133, Cs-134, Cs-137, Pm-147, Sm-151, Eu-152, Eu-154, Eu-155, etc.), as well as some uranium and transuranic elements (mainly Pu-238, Pu-239, Pu-240, Pu-241, Am-241, Am-243, Cm-242, Cm-243 and Cm-244), will arise as a result of fuel failures during operation of the reactor, or from traces of uranium carried into the core on fuel-element surfaces after fabrication.

Locations

The radionuclide content of irradiated graphite from nuclear reactor cores can arise from two sources: intrinsic and extrinsic. Intrinsic radioactivity results from the neutron activation of carbon and other stable impurities within the graphite structure. Frequently this will contribute the large majority of activity in i-graphite. Extrinsic radioactivity is the result of surface contamination from other components in the reactor circuit due to damage and corrosion; possible sources include fuel cladding, the pressure vessel, coolant gas and various other support structures. In some cases this contribution can be relatively large, as for AGRs which have been contaminated with cobalt-containing metal oxides within the reactor circuit leading to a significant further Co-60 contribution. An additional source of radioactivity, which may be of either an intrinsic or extrinsic origin, are fission products which will arise from both the fuel and the natural uranium impurity of the graphite (below 0.1ppm) when undergoing fission. The origin of the impurities will therefore determine the location of the radionuclides; an extrinsic origin will give rise to surface bound adsorbed radionuclides whereas an intrinsic origin will result in the radionuclide being 'trapped' either interstitially or intercalated inside the graphite structure (Figure 3).

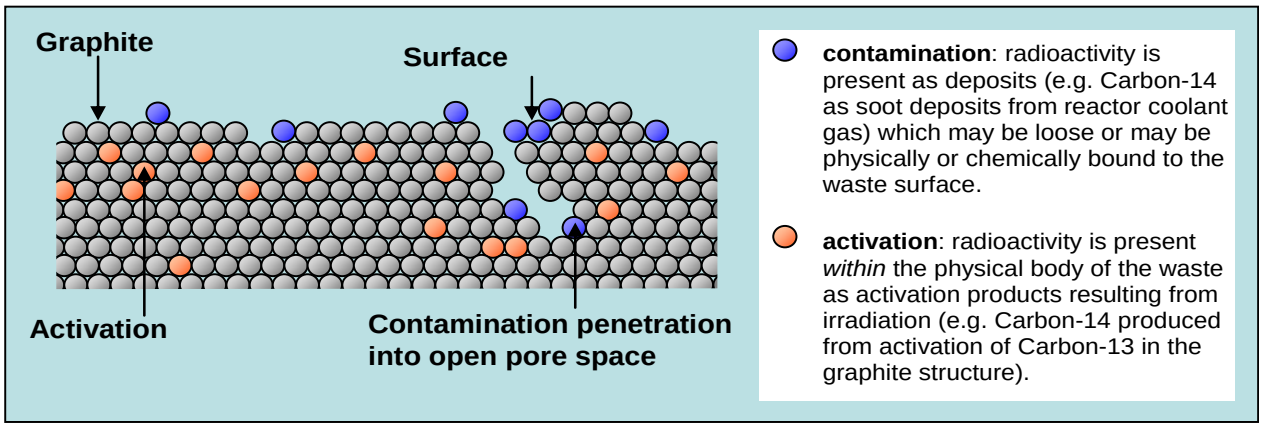

Figure 3 Schematic molecular cross-section of i-graphite showing typical distribution of contaminants

It may be possible, through the application of various treatment techniques to remove the surface radionuclides without compromising the structural integrity of the graphite; however any radionuclides which are located within the graphite structure will only be removed through the application of destructive techniques. Thus the characterisation of the impurities in the graphite is an important factor in determining the end of life radioactivity as well as the location, and therefore, the necessary treatment regime required for their removal.

Investigation of the location, speciation and bonding of radionuclides in graphite is complicated by the low concentration of radionuclides relative to carbon (< 1 ppm) and the difficulty in determining the location of radionuclides in the graphite structure. It has been considered that leaching or desorption of radionuclides out of graphite matrices (either by thermal or chemical treatments) is dependent on location and bonding mechanism.

Three main locations have been identified for radionuclide impurities in irradiated graphite: homogeneous distribution, concentrated "hotspots" and as a film on pore surfaces and in near surface layers. In the case of C-14, if it is covalently bound within the structure, its chemical form is elemental. It can be removed by oxidation if exposed at a surface (the latter two locations). Apparent thermal release may be due to oxidation by impurities on the surface or in the system.

Potential techniques for the treatment of i-graphite and the removal of contaminants are discussed in Section 6.

4 Graphite Management End Points

Defining the various targets (end points) for an integrated waste management approach allows analysis of the key stages of the road map (i.e. from in-reactor storage to final disposal) to be undertaken with regard to the most economic, environmental and sustainable options. This methodological approach will enable member states to select the most appropriate options to meet their specific criteria and considerations. Stage end points define stages throughout the road map, whereas the final end point defines graphite in its final destination.

The aims of the CARBOWASTE project have been aligned with the principles of the EU Waste Management Hierarchy (Figure 4), the key principle of which is to ensure that wastes are dealt with as high up the hierarchy as possible. Within this, it is recognised that, although the hierarchy holds true in general terms, there will be certain wastes for which the waste management options are limited or for which the option causing least environmental impact lies towards the bottom of the hierarchy. In deciding what the most appropriate disposal route is, both environmental and economic costs and benefits need to be considered. This decision should be reached taking into account all the costs and impacts associated with waste disposal, including those associated with the movement of waste.

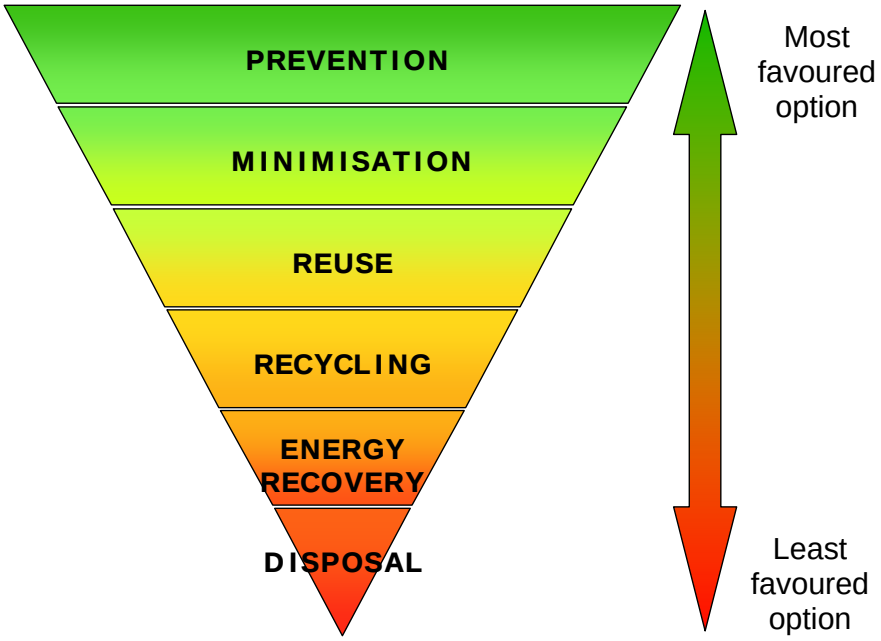

Figure 4 The Waste Management Hierarchy

Wherever possible the Proximity Principle should be applied. This recognises that transporting waste has environmental, social and economic costs so as a general rule, waste should be dealt with as near to the place of production as possible. This has the added benefit of raising awareness about waste and encouraging ownership of the problem at the local level.

4.1 Stage End Points

The definition of end points between the distinct stages in the processing of i-graphite assists with the definition of options for assessment within the MCDA. The three main processing stages are:

- retrieval and segregation;
- treatment; and
- disposal.

It is essential to clearly define these stages if evaluation of technology options is to be performed using MCDA, since a meaningful comparison can only be done by considering the same start and end points for each processing stage. The processing stages and associated end points are illustrated in Figure 5.

Throughout these processes, the radioactive inventory of graphite will change, due to radioactive decay. Additionally, the quantity and physical form of the graphite (both radioactive and non-radioactive components) may change. For example, underwater retrieval will lead to some leaching of radioisotopes into the water, generating a new waste stream that will require management. Treatment options may result in the generation of waste streams in liquid or gas phases, both radioactive and non-radioactive. The quantity and form of graphite consigned to disposal (if any) may be significantly different to that prior to retrieval.

The end points illustrated in Figure 5 are generic. Not all options for graphite management will include a treatment stage, for example. Some countries may elect to retrieve graphite and then package and dispose of it without any form of treatment or encapsulation/grouting. In the case of entombment or in-situ decommissioning, there is only one end point (with no intermediate stage end points); graphite in-situ is entombed, after which it is in its final destination.

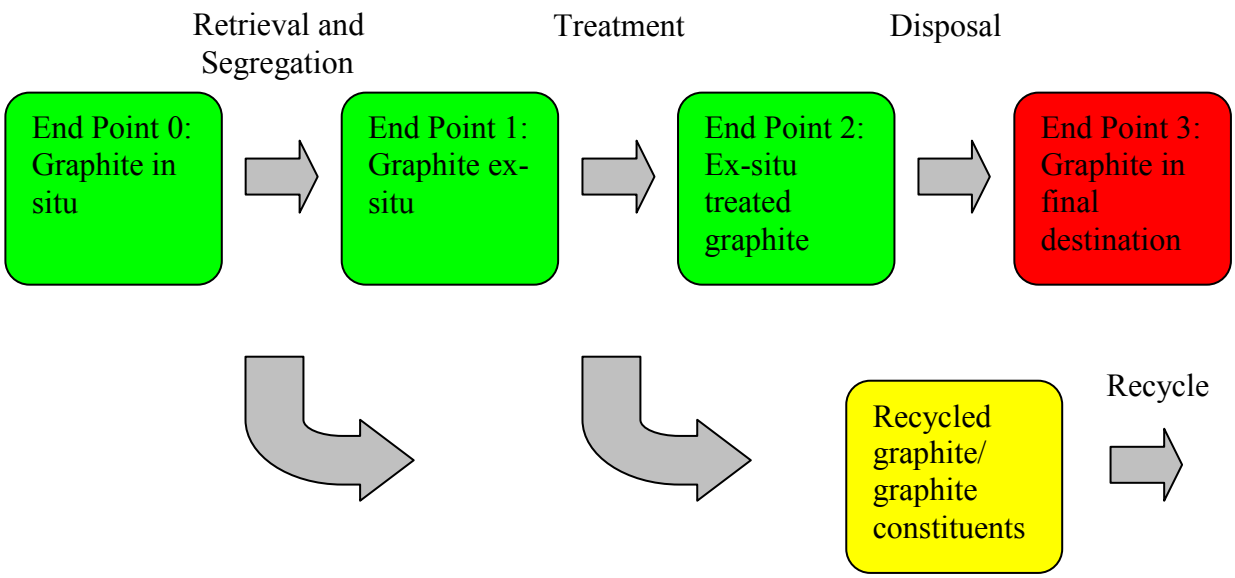

Figure 5 CARBOWASTE End Points

Retrieval and Segregation: End Point 0 to 1
The processing stages commence with the irradiated graphite in the reactor core, or in storage facilities. This is *END POINT 0: Graphite in-situ.* After a delay period of 0, 25, 50 or 75 years to allow decay in activity of many nuclides (these periods have been selected in the CARBOWASTE project to reflect the most likely retrieval scenarios), the graphite may be subjected to some form of in-situ treatment (noting that, currently, there are few realistic options for this). It is further noted that treatment processes at this, and subsequent processing stages, produce secondary wastes which will lead to additional waste, unless it can be recycled.

Retrieval and segregation of the graphite then commences; retrievals may be manual (if there has been sufficient radioactive decay to permit access), or may use remote handling devices, or some combination of the two. The graphite may be retrieved intact or in fragments.

In some cases the graphite is immediately transported to the next processing stage, but it is possible that some member states would elect for some form of interim storage at this stage. This could be within vaults or silos, during which cross-contamination from other waste materials might occur.

Reactor cores contain a wide range of non-graphite components such as thermocouples, securing wires and metallic connecting pins. Dependent on the planned treatment processes, these may need to be segregated from the graphite either at the point of retrieval or subsequently during the retrieval process. It is noted that operator doses during the retrievals process may be dominated by such materials and the surrounding reactor structure, and not necessarily by the i-graphite itself.

Ex-situ graphite, potentially segregated from non-graphite components, and following an optional interim storage period forms *END POINT 1: Graphite ex-situ.*

Treatment: End Point 1 to 2
The treatment phase commences with the graphite ex-situ, potentially following a period in an interim store. The graphite, if subject to ex-situ treatment, is then transferred to the treatment facility. This may be at a location remote from the original reactor/graphite waste store site. As with in-situ treatment there are a range of treatment techniques which may be deployed. The range of potential treatment technologies is likely to be much wider than those deployed in-situ.

Following treatment, as for the initial retrieval stage, there may be a period of interim storage prior to the next processing stage.

Ex-situ graphite, following treatment and, potentially, an interim storage period forms *END POINT 2: Ex-situ treated graphite*.

Disposal: End Point 2 to 3
The third, and final, stage encompasses the conditioning and disposal of the graphite. Conditioning includes processing the wasteform into a product that meets the waste acceptance criteria (WAC) for the receiving facility. If WAC are not available at the time of treatment and/or packaging, there is a risk that a future disposal concept would dictate further treatment or repackaging of graphite.

The final end point for the graphite is *End Point 3: Graphite in final destination* (see Section 4.2).

Recycle and Re-use
The retrieval, treatment and disposal stages each manage graphite, or graphite constituents, which could potentially be recycled or re-used. This includes:

- graphite bricks and tiles;
- graphite constituents e.g. C-14; and
- materials for potential re-use/recycle.

4.2 Final End Points

The final end point in the road map defines graphite in its final destination. Many approaches to i-graphite management include the disposal of some material within a repository (either near-surface or deep geological). Treatment or destruction methods (such as incineration) might reduce the volume of material to be consigned to a repository significantly. Other, more total, destructive techniques might release the entire i-graphite to the atmosphere, which would represent the final end point. An approach of indefinite storage could in some circumstances be viewed as a final end point.

In cases where member states determine, and proceed with, intermediate process stages prior to determining a final end point, this may restrict the number of options available for the final end point. For example, if graphite is retrieved and packaged for disposal without any form of treatment, this may preclude disposal options other than a deep geological repository. Conversely, in cases where a final end point for graphite is determined as part of a national strategy, this could limit the number of options for intermediate processing stages. For example, if a member state made the decision for graphite to be disposed of in a near-surface or at-surface facility, this would likely influence the required treatment / encapsulation / or packaging requirements of the graphite.

5 Retrieval and Segregation Techniques

The first active stage of i-graphite management is the removal of graphite from the reactor core via a process of retrieval, which could include simultaneous segregation. Every reactor has different assembly characteristics and the operational conditions of graphite and other carbonaceous material will vary from reactor to reactor. The integration of the graphite fixing and support in the core as well as measuring devices creates diverse 'gangue' material which is mixed with the extracted waste and may need to be separated into different waste streams for treatment or disposal. The nature of segregation to be undertaken will impact on the removal techniques, and the environmental conditions required to achieve this may be challenging.

Retrieval and segregation of i-graphite, if part of a greater nuclear plant decommissioning project, cannot be considered in isolation but must be integrated with the total project activity. Prior to retrieval and segregation, a preliminary waste route must be determined, which is defined as:

> *The immediate route for i-graphite and other materials removed from a reactor or other non-conditioned waste store but prior to its conditioning / packaging for transport away from the vicinity of the reactor to an interim store or disposal site* (Doosan Babcock, 2012).

Once a preliminary waste route (and ideally some or all further downstream operations, such as storage, packaging, treatment, or disposal) has been determined, an approach to retrieval and segregation can be implemented.

The following retrieval and segregation scenarios have been identified that used, singly or in combination, will affect the quality, quantity and form of the primary i-graphite and secondary waste produced.

1) Graphite retrieved in-air
2) Graphite retrieved under-water
3) Graphite retrieved in an inert atmosphere
4) Graphite retrieved as bulk blocks
5) Graphite retrieved in a particulate form
6) Segregation of graphite undertaken in-situ
7) Segregation of graphite undertaken following retrieval
8) Segregation undertaken at component level
9) Segregation undertaken at contaminant level

Due to constraints of safety, feasibility, economics, access routes to the i-graphite, radiation environment, structural integrity, and infrastructure, not all of these are necessarily practicable in specific applications. Additionally, due to the variation in the physical properties of the graphite (e.g. condition and quality) that might be encountered in a single reactor core, a combination of a number of these scenarios might be necessary.

5.1 Factors Affecting Retrieval and Segregation Options

There are many potential factors that could affect the range of suitable options for i-graphite retrieval and segregation, including those arising from being part of a greater nuclear plant decommissioning project. Key variations in retrieval approach will include the duration of *in-situ* storage prior to retrieval and the nature of retrieval method, such as the level of remote vs. manual retrieval and retrieval in bulk blocks, or in particulate form. Two key factors that will impact the approach to retrieval are the reactor containment and core design, and the graphite condition.

Reactor Containment and Core Design
This will impact upon the mode of access into and out of the reactor containment, the state and conditions inside the reactor containment once access has been achieved and the components likely to be encountered. Even amongst common reactor designs, such as Magnox, UNGG, RBMK etc, variations will exist. Those with particularly limited access might require retrieval of graphite via remote manipulator.

The option of flooding the core to provide a radiological barrier is an option for reactors where water-tight containment, such as a pre-stressed concrete reactor vessel, exists.

Graphite Condition
The quality, quantity, configuration and radioactive inventory of graphite within a reactor core will influence the available retrieval options. A key consideration is the dose that would be received by operators during retrievals due to the residual radioactivity present in the core. This radioactivity is present in the bulk graphite, gangue material and potentially in the form of contamination from fuel failure and in the surrounding reactor structure.

Doses received by operators during retrievals could be reduced by the greater use of remote, automated techniques. It is possible that this would be required to achieve safe operating doses and an acceptable level of conventional safety. A period of in-reactor storage, i.e. a delay to retrievals, can reduce doses to some extent by allowing the radioactive decay of shorter-lived radionuclides, such as Co-60. Doses could also be reduced by use of temporary (e.g. water or other introduced materials) or incidental shielding that can be opportunistically used to manage dose.

For cases of retrieval after a short delay period there would be a requirement towards fully remote or fully shielded environments (e.g. underwater), with the opportunity to move towards semi-remote or even some manual operations after a prolonged delay period. The benefits of delaying retrieval of graphite must be balanced against the gradual reduction in the structural integrity of the reactor core (and containment structures), which will occur with time. Additionally, knowledge and skills may be lost with time.

5.2 International Experience

The design and methodology for retrieving i-graphite can draw upon the knowledge gained on existing or completed projects: -

- Windscale AGR (WAGR), a prototype Advanced Gas Cooled Reactor in the UK, decommissioned with i-graphite removed in air remotely using an externally mounted remote dismantling machine.
- Graphite Low Energy Experimental Pile (GLEEP) in the UK, decommissioned, graphite removed in air mechanically using winches and baskets with manual intervention. Graphite was crushed prior to dispatch.
- Fort Saint Vrain (FSV), a High-Temperature Reactor with a prestressed-concrete pressure vessel, was filled with water after the pressure vessel top was cut to get access to the core internals. The nuclear island has been totally removed.
- Bugey Uranium Naturel Graphite Gaz (UNGG) Reactor in France, closed but with a well developed design phase for removal underwater assisted by manually operated tools and lifting baskets from a moveable platform (using a similar approach to that used for FSV).
- Leningrad RBMK, a high power channel reactor, in which i-graphite was removed during a repair activity mid operational life using a process route.
- Vandellos Silo, an operational waste storage facility part of a prototype reactor in Spain, similar to a French UNGG, in which operational i-graphite wastes stored in a Silo were retrieved and packaged.
- Brookhaven Graphite Research Reactor in the USA; i-graphite was removed in air using remote excavation methods.
- AVR experimental High-Temperature Reactor in Germany is being grouted with light concrete to allow removal of the i-graphite internals together with the whole steel pressure vessel for subsequent interim storage.

5.3 Retrieval Options

One option for the removal of irradiated graphite from nuclear reactors is to dismantle the core by removing the blocks individually, one at a time. This approach to graphite retrieval has been undertaken successfully on WAGR. A combination of ball grab (for graphite blocks with holes already present), drill and tap, grabs, sweeping brushes and vacuum devices were employed in the dismantlement. A similar process of drill and tap was used in the decommissioning of GLEEP (Doosan Babcock, 2012). Additionally, intact groups of blocks might be removed together. Block removal may present difficulties relating to dealing with cracked, broken or clamped blocks, which are a by-product of degradation, weight loss, increased porosity and dimensional change of the graphite during its life within a reactor. For conventional retrieval methods this might require significant additions to the retrieval tooling selection to enable the various complexities to be addressed.

A more recent example of graphite retrieval is that of the Brookhaven Graphite Research Reactor in the USA, in which an excavator was deployed within the bioshield to remove (via a process of ‘mining’ or excavating) over 60,000 graphite blocks. This approach involves breaking up the graphite prior to its removal in baskets.

The proposed nibble and vacuum approach takes the excavation approach one stage further, through further minimising the tooling requirements and simplifying the retrieval approach. The technique

involves removal of the high-dose components in the reactor core by size-reducing in-situ ("nibble") followed by removal from the reactor core by suspension in air or nitrogen via a vacuum retrieval system ("vacuum"). This approach to graphite retrieval would require no modification in approach to address the potential issues of bulk retrieval listed above, as it would size reduce the graphite and then vacuum it out of the reactor with no requirement for additional tooling (EPRI 2010).

Retrieval of graphite stored in the Vandellos vault comprised a remote manipulator with petal grab tool to grab graphite pieces and load into bags. This was supported by a spade tool for pushing and loading and a rake tool for rearranging, pulling and loading.

Underwater retrieval has been demonstrated during the decommissioning of Fort St Vrain and is in preparation for Bugey. This technique allows proximity to the workface, with good line of sight, personnel shielding and the creation of the opportunity to use simple manual tooling. Dust management is also facilitated.

5.4 Segregation Options

Segregation might be implemented during the retrieval process, or at some point following this, prior to treatment or packaging, for example. Gangue components that are attached or associated with the graphite may be segregated, since they may require an alternative treatment procedure or disposal route, primarily due to the presence of activation products imparting a level of radioactivity greater than that of the bulk graphite. It is possible that no segregation will occur, as in the case of WAGR.

Graphite components themselves might be segregated since a single waste management approach might not be suitable for the entire graphite inventory associated with a reactor. Some blocks are moderators, some reflectors, some contain channels and some graphite is used in thermal columns. Segregation of graphite is likely to be driven via the need to separate materials of different levels of radioactivity. A proportion of graphite with very low levels of radioactivity might be suitable for a reuse or recycle option, for example, while graphite with higher levels of radioactivity may only be suitable for disposal, or may require treatment before disposal.

Graphite segregation processes could include:

- Selective removal of i-graphite from different parts of the core taking account of variations of activity within the core. It is generally understood that maximum radioactivity levels are in those blocks nearest to the centre of the core;
- Sorting of graphite outside in an extension to or outside of the reactor containment prior to dispatch; and
- Segregation by splitting of individual graphite blocks into parts of different specific radioactivity.

6 Treatment Processes

6.1 Introduction

Treatment of i-graphite may be undertaken for a variety of reasons, including, for example, volume reduction, diversion of activity/volume from a geological repository, reclassification (e.g. from Intermediate Level Waste (ILW) to Low Level Waste (LLW)) or to meet regulatory constraints. In this section, potential treatments for i-graphite are examined and possible drivers for the choice of each specific treatment type are discussed.

6.2 Potential Treatment Processes

Decontamination processes are critical for removing a substantial proportion of the radionuclide inventory, simplifying the inclusion of carbonaceous materials within an industrial recycling process. They also dictate the form and properties of the end product, and define the form and nature of the waste streams produced.

The desired end-point for i-graphite can have a large influence on the choice of treatment process. For example, waste acceptance criteria for a near-surface disposal facility are likely to place more rigorous constraints on activity levels than for a deep geological facility due to shorter pathways to the external environment and lower residence times. Therefore i-graphite to be routed to a near-surface disposal facility may require more significant decontamination prior to packaging and disposal.

I-graphite treatment processes include gasification (steam reforming or oxidation with capture of volatile radionuclides and collection of residues), decontamination by 'roasting' (partial decontamination by selective removal of surface-located radionuclides under an inert atmosphere), carbon re-deposition following gasification (effectively reversal of gasification-producing products with residual activity suitable for reuse in the nuclear industry), chemical decontamination (unproven for large volumes but with the potential for reducing the radionuclide inventory), intercalation/exfoliation (increasing accessible surface area for radionuclide removal by another process) and direct reuse (shuffling components within a reactor to maximise useful life or use expended component as raw material for a new component).

Treatment processes can be loosely classified as thermal or chemical, although it is recognised that some processes can cross over these two groups (e.g. steam reformation), often combining elements of the two.

Thermal Treatment Processes
In simple terms, thermal treatments involve heating the graphite in an inert atmosphere to a sufficiently high temperature such that the adsorbed reactive gases on the graphite structure will react with adsorbed radioisotopes or initiate pyrolysis effects breaking chemical bonds. Alternatively, this process can be performed in diluted reactive gases such as oxygen, steam, carbon dioxide, or hydrogen to drive the more mobile/volatile contaminants off (e.g. with steam reformation).

Heating graphite can, at least in some cases, lead to selective loss of isotopes (particularly H-3 and C-14) from the graphite structure, which can either be a physical or chemical process. This phenomenon has the potential to be utilised both for a form of partial decontamination of graphite and for the production of a fraction of gas concentrated in radioisotopes for particular recycle opportunities.
Graphite has a porous structure. A proportion of the pore volume is open, meaning it is connected with the gas atmosphere in which the graphite resides. During operation with graphite in a reactor core, isotopes such as C-14 and H-3 may accumulate on the surface of the pores through a variety of possible mechanisms:

- Isotopes formed in the bulk gas phase may diffuse into the pore volume and deposit on the pore surfaces.
- Species absorbed on the surface of the pores during manufacture, or during exposure of the graphite in air, may be activated in the neutron flux.

Any of the above mechanisms may yield a pore surface layer enriched in radioactive isotopes, which might then be released by gasification, by heating either in an inert atmosphere or one which encourages gasification of carbon, such as steam. Figure 6 shows a rather high fractional release of radiocarbon for i-graphite (~10%) with comparatively small mass losses (~0.5%). It is important to note that the limitation in the C-14 releases is due to the exhaustion of oxidants. Therefore, it has been proposed to repeat this treatment, by reloading the pore system with oxidants before performing successive heat treatment to achieve higher decontamination.

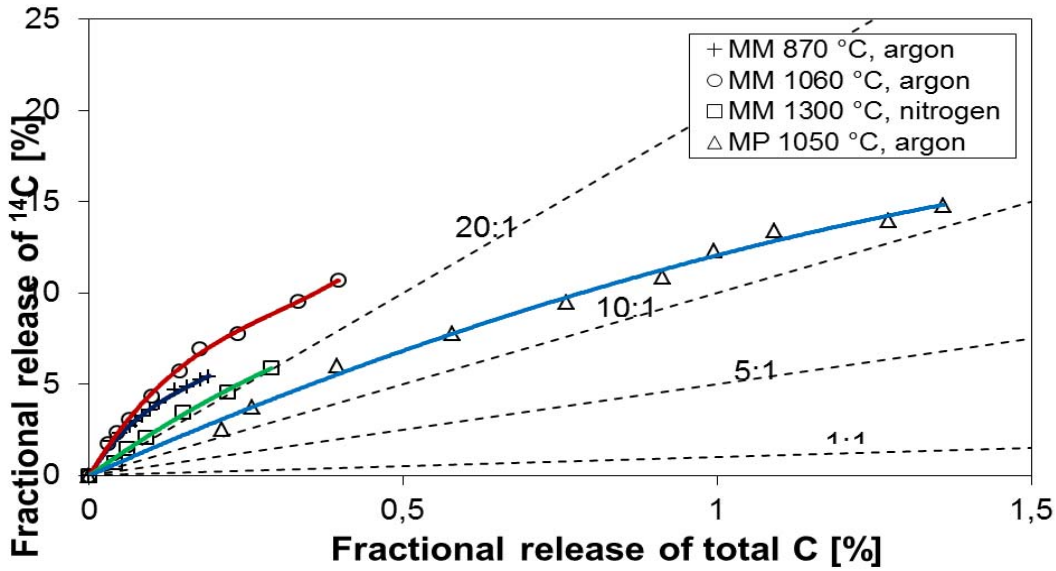

Figure 6: Fractional release of radiocarbon during 'Roasting' (MERLIN Massive (MM) or Powdered (MP) samples)

Whilst such processes generally remove only a small fraction of the graphite, the portion released may contain a significant proportion of the radioactive isotope inventory – effectively partially decontaminating the graphite. Unfortunately, there are likely to be limitations on what can be achieved by roasting. Some of the contamination mechanisms will be relevant to the closed pores which may not release their inventory during the heating procedure. Furthermore there are isotopes formed by activation of bulk materials and impurities in the graphite during reactor operations.

Enhanced release will not be possible for the isotopes that are locked into the non-porous graphite matrix, without higher corrosion to open a further part of the closed pores.

The in-situ heat treatment of graphite is another interesting idea, which might allow the release of significant radionuclide inventory from the intact moderator of a reactor. There are three problems to be overcome with this on an industrially practical scale. The first is that the intact reactor core and coolant circuit materials are designed to operate in a closely defined range of parameters (particularly temperature and pressure), and this gives little room for safely achieving the deviations necessary to release significant quantities of radionuclides in a short time. The second limitation is that a significant amount of the legacy graphite exists within reactors which have been shut down for too long to permit such a process to be applied. This is because the equipment for gas circulation and containment is no longer functional. With the passage of time the proportion of legacy reactors in this state will increase. Finally, volatile species may be discharged by *in-situ* heat treatment and appropriate consents to discharge must be obtained and abatement equipment performance demonstrated.

An example of practical experience in the thermal treatment and disposal of nuclear graphite can be found in the case of GLEEP (Bradbury *et al.*, 2004). No radiological characterisation parameters are documented in this report; however GLEEP graphite is reported as LLW. The successful disposal of graphite from the GLEEP reactor using this methodology indicates graphite decommissioning using thermal treatment is a viable option. GLEEP graphite blocks were thermally treated in an industrial incinerator at 1423K for approximately 3 hours under a forced air supply. It is noted there is also the presence of other miscellaneous waste within the incinerator. Typically, 87% of H-3 and 63% C-14 activity were removed from each block and a very crude net weight loss assessment of 6% calculated post-treatment.

Chemical Treatment Processes

Chemicals can decontaminate graphite by selectively removing the surface layer and by destroying the binder material. Based upon studies using mineral acids, alkaline solutions, dissolved oxidising agents, organic washing detergents or such combinations, two possibilities for decontamination of the surface layer of graphite material were identified. A mild combination solution destroys the binder material and dissolves a minimal amount of graphite resulting in the removal of surface material. A more aggressive approach using electrochemical technology not only destroys the binder material, but also dissolves graphite surface material, resulting in the removal of the surface graphite layer as a decontamination step.

Chemical leaching tests have been made on BEPO and Magnox reactor graphites to determine the release rates and mobility of C-14 and H-3 (McDermott, 2012).

- An acidic environment yielded the highest release activities for both radionuclides. No change in pH was observed in any of the leaching experiments.
- C-14 is present in leachable and non-leachable forms. Intercalation with penetration of interlayer spaces within the graphite structure is thought to be the mechanism behind C-14 removal.
- Hydrogen ion isotopic exchange is thought to be the mechanism behind H-3 release.

- Steady state of release was achieved under all conditions by day 90. After this, very limited amounts of both H-3 and C-14 were released.

The chemical treatment process removing mobile and accessible H-3 and C-14 prior to decommissioning or repository storage shows that a significant portion of both radionuclides remains within the graphite structure. Even harsh oxidising and acidic environments have failed to remove more than 30% of the radionuclides. Thus, it can be concluded that this part of the radionuclides are strongly bonded within the graphite matrix and potentially resistant even to long-term leaching. In terms of using this methodology as a pre treatment method the industrial and financial feasibility of these processes would need to be evaluated in more detail and with consideration of the i-graphite characteristics.

An investigation has been undertaken of the chemical removal of Co-60, Eu-152 and Eu-154 from the graphite irradiated in the TRIGA reactor using different acids at various concentrations. Removal efficiencies using sulphuric acid ranged between 70 and 90%. A mixture of nitric acid 65% and phosphoric acid 85% (1:1) led to removal efficiencies ranging between 60 and 86% with the most efficient removal achieved for Co-60 in each case.

The bulk of i-graphite samples analysed have revealed the distribution of activated elements to be mainly in the closed porosity or between the graphite layers, not involving chemical bonds (Capone *et al*., 2013). It is therefore possible to separate the graphene layers using a suitable intercalating solvent, which can then reach the inner layers/areas (i.e. closed pores, crystallites, etc.) and extract the contaminants in solution.

The intercalation process involves applying an organic solvent (e.g. N-Methyl-2-pyrrolidone) to produce unfunctionalised and non-oxidised graphene layers in a stable homogeneous dispersion. The dipole interaction between graphenes and organic solvents facilitates separation of the layers in a regular manner and, assisted by mild ultrasound, results in a dispersion of the graphite in a workable medium. This enables processing, treatment and easy characterisation for contaminant recovery (Figure 6).

Importantly, neither oxidation nor any strong acid action takes place, so that the graphite can be completely recovered. After separation from the organic solution containing the contaminants the non-oxidised graphene/exfoliate powdered graphite may be useful in both research and industry.

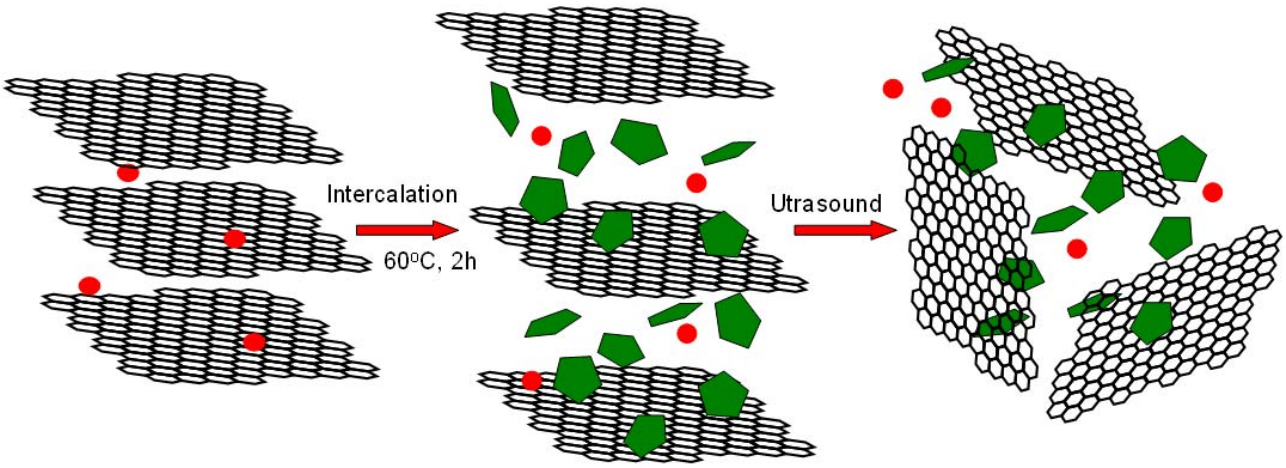

Figure 6 Representation of the main steps in graphite exfoliation by organic solvent and ultrasound

Steam reformation transforms graphite fragments by high temperature interaction with steam into two combustible gases (hydrogen and carbon monoxide) as follows:

$$C + H_2O \rightarrow CO + H_2$$

After oxidation and transformation into CO_2 and H_2O, the gas is released to the atmosphere through a High Efficiency Particulate Air (HEPA) filter (IAEA, 2006).

If the carbon in graphite is completely gasified (e.g. by steam reformation or air oxidation) the remaining non-volatile isotopes will be left behind as a residue, while semi-volatile isotopes (such as Cs-137) may be collected with the non-volatile ones, or in adjacent low temperature zones. This behaviour has been confirmed in a study by Jülich (Podruzhina, 2004). Total gasification provides the means to collect these isotopes in a concentrated form for waste management. This is a significant outcome, since the non- and semi-volatile isotopes include all the principal gamma-emitting ones. This allows all further downstream operations with the gas stream to be performed "hands on". The separation of volatile non-carbon isotopes such as H-3 and Cl-36 can be readily accomplished during gas phase processing: for example H-3 can be converted to water and separated from the off-gas, carbon dioxide; this off-gas could be incorporated with future carbon sequestration programmes.

It is not certain that the early deliberate release of the C-14 content of i-graphite to the atmosphere would be radiologically acceptable. However, if the graphite is to be dispersed in gaseous form in the atmosphere, it is essential to minimise the release of any non-carbon isotopes such as H-3, Fe-55 and Co-60. This implies a requirement for the efficient gasification of the carbon and its separation from other radioactive residues.

Another potential option would be to react the resultant carbon dioxide with calcium or magnesium oxide, hydroxide or metal to form a stable carbonate solid, which prevents the release of radionuclides into the atmosphere. The resultant solid would have greater volume than the original graphite; e.g. it is estimated that 1 tonne of graphite could be transformed into around 8 tonnes of calcium carbonate or 16 tonnes of barium carbonate. However, if this solid were pelletised, it could

be used as void in-fill in grouting of other radioactive waste. A particularly interesting possibility at Magnox reactors is to use the Magnox fuel cladding or splitter waste as the source of magnesium for this option, thereby dealing with two radioactive wastes in just one waste form.

In Russia, a graphite immobilisation process has been developed, known as the Self-Propagating High Temperature Synthesis (SHS) process, similar to the thermite reaction, in which graphite is mixed in stoichiometric proportions with aluminium and titanium oxide according to the equation:

$$3C + 4Al + 3TiO_2 = 2Al_2O_3 + 3TiC$$

The reaction is initiated electrically and is thereafter self-propagating. It has the advantage of immobilising all significant isotopes present in the oxide and carbide matrices (including C-14 in the latter) and results in a highly unreactive and insoluble product with very good leaching characteristics (IAEA, 2006).

Treatment for recycle/reuse

Seven recycle/reuse processes have been investigated within CARBOWASTE:

- Graphite recycle to nuclear grade graphite;
- Graphite recycle to electrodes for waste vitrification;
- Graphite recycle into silicon carbide;
- Graphite reuse for decontamination of waste streams;
- Direct reuse of graphite for various applications;
- Isotope separation; and
- C-14 recycle and supply.

The presence of the isotope C-14 is usually considered a problem in the management of irradiated graphite waste. However, the isotope is used in many applications of chemistry and medicine in quite significant quantities. In order to achieve such recycling, two developments would need to take place. First there needs to be an efficient means of separating the C-14 from the graphite, and second the resulting product needs to have the right characteristics of chemical form, isotopic purity and quantity for supply to the market. It also needs to be economically attractive to consumers.

At the beginning of CARBOWASTE there had been no significant endeavours in respect of irradiated graphite reuse/recycle. Over the 5-year duration of the project, significant developments in this field have been made both within CARBOWASTE and other related projects (e.g. US DoE Deep Burn Project) which have provided valuable insight and supporting data to substantiate irradiated graphite reuse/recycle opportunities across the nuclear industry.

The potential industrial recycle of C-14 over a number of years could use a significant proportion of the total i-graphite inventory, although it is most unlikely that most or all C-14 in irradiated graphite could be recycled. For example one UK manufacturer of products annually uses approximately 0.3% of the inventory of the UK's Magnox reactors. Although C-14 is produced for manufacturers by reactor irradiation of nitrogen species and hence is available to them in high isotopic purity, a lower specific activity (i.e. isotopic dilution) could be acceptable to manufacturers as input material for some applications.

The possibility of recycling material directly from irradiated graphite (without isotope separation) has been examined. This would involve using 'roasting' techniques to produce a fraction with the highest possible C-14 content, and selecting graphite with the highest possible C-14 activity for recycle. It is concluded that the gap is probably too large to bridge without some purification by isotope separation, which has been deemed impractical (Bradbury and Goodwin, 2013).

The Silicon Carbide (SiC) process has the potential to use graphite to replace grout or other encapsulants in immobilising other wastes. This is likely to be dependent on a significant qualification programme to determine suitable candidate wastes.

All of these processes require further development, and the studies have shown that the large-scale application of these processes is generally not economically viable. Small-scale diversion of appropriate material through these processes is possible, but the impact on repository size for the remainder would be insignificant.

6.3 Experimentation

The majority of decontamination processes for irradiated nuclear graphite are currently at the experimental stage. Techniques under investigation include pure thermal, oxidation and aqueous treatment processes.

A significant part of the CARBOWASTE experimental programme has involved experiments designed to determine the potential for selective release of radionuclides from irradiated graphite.

The results show that it is frequently possible to achieve selective release of radionuclides in a gas or a liquid phase, while leaving the remaining graphite as a solid.

Most of the experiments carried out so far have been on a very small (laboratory) scale; however, the "scalability" of the results for application in a large scale industrial process will require further investigation.

The two principal issues to be addressed relate to:

- the practicality of applying the processes which have so far been demonstrated on lab scale; and
- the adequacy or otherwise of the decontamination performance achieved so far to underpin an industrially useful performance.

The experiments performed have used generally very simple equipment for the heat treatment of irradiated graphite in a static or flowing gas or liquid phase chemical decontamination of graphite. The industrial-scale heat treatment of graphite is currently being developed, and the adaptation of the process to use different gas mixtures, contact times, particle sizes (and similar parameters) to match the lab scale experiments should be relatively easily accomplished. Likewise the chemical decontamination of graphite in aqueous-based environments should be relatively easily accomplished in conventional industrially-available contacting equipment. What will need to be considered carefully in this latter case is the management of potentially hazardous liquid waste arising from the process.

Experiments performed on the efficiency of i-graphite roasting have led to the conclusion that, however carefully it is optimised, it is unlikely that more than about 60% of the C-14 and 80% of the H-3 can be released in the first few per cent of carbon lost (Podruzhina, 2004). This observation is confirmed by preliminary work on blocks removed from the UK GLEEP reactor.

The electrochemical treatment of graphite causing it to exfoliate has potential to allow significant decontamination. However, while this procedure is easy to demonstrate on a lab scale there are difficulties to overcome in achieving industrial practicality of this process.

Carbon isotope separation was studied as part of the WP5 work package. While significant efforts were made to define potentially practical and cost effective options for this, in the end no such options were identified.

Scientists are naturally interested in phenomena which show any form of selective release of radionuclides, particularly the selective release of individual carbon isotopes. It is recognised that many of the processes demonstrating a reduction in the activities of key radioisotope contaminants may be of use at some level within the waste management hierarchy; whether the objective be to reclassify the i-graphite to a level where more cost-effective disposal options can be considered (e.g. from intermediate to low level waste, which may only require a small reduction in activity) or to fully decontaminate for re-use / recycle applications. Whereas industrial practicality can easily be foreseen for the simple decontamination processes thus far tested on lab scale, the application of each process will ultimately depend on the required decontamination efficiency.

7 Disposal Assessments

7.1 Introduction

Disposal of radioactive waste forms a key part of international policy for long-term radioactive waste management. Disposal can be implemented by isolating the waste from the biosphere in a surface disposal facility (SDF), or in deep geological disposal facility (GDF). The irradiated graphite waste itself, whether treated or not, will likely be encapsulated in waste packages as part of the disposal process, which further provides for long term stability. Disposal facilities are designed such that they do not require active radioprotection measures and are passively safe, based on the performance of manmade and natural barriers to provide containment and isolation of the waste, and ensure any radionuclide transfer back to the environment is radiologically insignificant.

In order to assess whether irradiated graphite can be disposed of as waste with or without further treatment, either in an SDF or a GDF, its behaviour under disposal conditions needs to be assessed. Disposal conditions are influenced by the natural hydrogeological environment and by the waste package and other engineered barrier systems (EBS). It must be assured that any radiological risk arising from a potential release of irradiated graphite derived radionuclides to the biosphere meets regulatory criteria. Scenarios have to be developed to consider if and how groundwater could come in contact with the disposed waste product. Processes by which waste-derived radionuclides might enter any groundwater pathway have to be considered, as well as processes affecting any subsequent radionuclide migration in groundwater to the biosphere, and biosphere processes that could result in a radiological dose to humans or flora and fauna. Migration from a disposal facility of irradiated graphite-derived radionuclides in a gas phase also needs consideration.

7.2 Radionuclide Releases under Repository Conditions

Graphite is a highly porous medium. Much of the radioactive inventory is only accessible for aqueous leaching and release upon water permeating the i-graphite porosity. Studies within the CARBOWASTE project have shown that in absence of hydraulic gradients, water permeation into the porosity of non-irradiated graphite is relatively slow and seems to be controlled by a diffusion process. However, irradiation increases the kinetics and the permeation rate. The results of the studies show that for disposal-relevant time periods, water permeation is rapid and does not limit radionuclide release. In the presence of only weak hydraulic gradients in a repository, water transport in the irradiated graphite is controlled by advection and in absence of hydraulic gradients by diffusion.

Radionuclide leaching behaviour was studied under a range of disposal conditions in order to quantify the long-term release of radionuclides after water ingress in the repository and into irradiated graphite products. The studies were carried out on irradiated graphite from CO_2-cooled Magnox (UK) and UNGG (France) reactors (Comte *et al*., 2013). Operational waste (such as graphite sleeves) was not studied.

Cl-36 release from the graphite waste into groundwater occurs in two stages. The first stage shows very rapid Cl-36 release kinetics (labile fraction) with a rate governed by diffusion through graphite porosity. Diffusion coefficients are in the order of 10^{-11} to 10^{-12} m^2/s. The second stage shows slow

Cl-36 release kinetics (non-labile fraction). The higher the reactor operating temperature, the lower the Cl-36 release rate of the resulting graphite waste into water. This may be due to the fact that with increasing temperature a significant part of the labile fraction of Cl-36 has already been released in the reactor. On the whole, the total amount of Cl-36 released varies widely, ranging from a few % to around 90% of the initial inventory. Leached Cl occurs mainly in form of chloride ions but chlorite was observed as well. Chloride ions show low retention behaviour in the geosphere. Cl-36 release is principally by advective transport with low retardation, and it has been shown that low permeability options (e.g. clay) may slow Cl-36 release by several orders of magnitude.

C-14 release in solution was always found to be low compared to Cl-36, with a rapid initial release followed by near stabilisation. The two stages of release of C-14 may be related to two different mechanisms of production in the reactor (N-14 activation of surface-adsorbed air versus C-13 activation of graphite structure). However, no difference was observed for air-cooled piles compared to CO_2-cooled reactors. In contrast to Cl-36, release rates of C-14 are not controlled by diffusion in graphite pores. The chemical form of released C-14 strongly affects the migration properties in the repository and surrounding geology. It may be in gaseous or dissolved form, organic or inorganic. C-14 is found to be mainly released in solution. Gaseous species represent less than 0.01 % of the total C-14 activity and are only detected as organic species. Inorganic forms (CO_2, CO_3^{2-}, HCO_3^-) are strongly retained within cementitious materials by sorption and incorporation in cement phases, whereas organic species are much more mobile, all the more so since they can be released as gaseous species.

The disposal properties of irradiated graphite waste can largely be improved by emplacement in suitable waste packages. For example, the French design considers emplacing graphite waste in metal carts which are then put into concrete containers. Cement or mortar would then be injected into the container, which would be completely closed with a concrete cap. Concrete and cement-based materials can play an important role, as a barrier against access of groundwater as well as against migration of radionuclides away from the waste. Cement is also used in Spain as engineered barrier material. It was shown that graphite powder is mechanically compatible with cement pastes. A particular problem is graphite dust and coated particles from HTR reactors. Special encapsulation is necessary to provide for stable waste matrices. In the CARBOWASTE project, three methods were successfully tested: encapsulation in cement, in cold ceramics and in glass.

The efficacy of products specially manufactured to stabilise carbon in a radioactive waste disposal site, or to act as confinement or packing material for other wastes and thermal management, in a repository environment has been examined. The stability of SiC formed from graphite and irradiated graphite has been studied under repository conditions, representative for either in an evaporite (salt), fractured hard rock (e.g. granite) or clay rock. The measured activity of C-14 leached from irradiated graphite is higher than the activity of C-14 leached from the SiC made from this graphite. Based on this, it seems that the transformation of irradiated graphite to silicon carbide could be a way of decreasing the C-14 release from the material. Because of a limited amount of irradiated graphite available for leach-testing compared to the amount of SiC that was used, further tests would be needed to confirm that SiC formed from irradiated graphite could be a suitable product that has a lower C-14 release rate.

By "vitrification", the porosity of i-graphite could be closed and i-graphite could be transferred into long term stable impermeable alternative waste matrix which would inhibit ingress of water and therefore allow for safe final disposal.

7.3 Repository Performance

The long-term performances of the various packaging concepts under repository conditions are assessed by determining their capacity to retain radionuclides. Retention values indicate if a diffusive front of radionuclides through a barrier such as cement could be delayed by hydrodynamic and chemical processes. Retention properties depend on the mineralogical composition of the cementitious materials, their alteration state, the kinetics and reversibility of retention and the geochemical conditions of the water.

The implementation of irradiated graphite disposal in an SDF or a GDF requires the demonstration that such a facility would be safe during both the operational period and after it has been sealed and closed. A safety case is used to demonstrate understanding of environmental safety and to address regulator guidance on what is required to permit the development of an SDF or a GDF. Quantitative studies of post-closure evolution in a safety case focus on how safety is provided for radionuclides that might dissolve in and be transported by groundwater after an SDF or a GDF is closed. After closure, this is the most likely way for radionuclides to reach those parts of the environment in contact with or readily available for use by humans (the accessible environment). However, other processes that could lead to the release of radionuclides to the accessible environment in the post-closure period, including gas-phase transport and human intrusion, could also be considered.

Assessment studies have been undertaken as part of CARBOWASTE for representative shallow and deep geological disposal facilities in the context of respective national waste policy, national regulations and national graphite waste inventory (Grambow *et al.*, 2013). For the calculations undertaken as part of a safety case, the performance of the barriers is often represented in a simplified manner although the specific approach taken in any national programme is frequently driven by the maturity of the programme and national regulations. Thus it is possible to identify and vary the key model parameters that represent the key Features, Events and Processes (FEPs), in order to understand and illustrate the potential radiological impacts of disposing of the inventory using different types of waste container in different kinds of geological environment. These calculations indicate the barrier performance requirements for different possible disposal concepts that would enable an implementer to satisfy radiological protection requirements. This gives confidence that a safe SDF or GDF could be designed.

In one specific study (Paksy *et al.*, 2012), four main scenarios with variants were identified as representative of the range of planned European disposal facilities:

1. Shallow facility (clay and hard rock variants);
2. Deep facility in argillaceous sediments (clay);
3. Deep facility in hard rock (both crystalline and sedimentary types); and
4. Deep facility in evaporite host rock (salt).

The Engineered Barrier System (EBS, e.g. containers, encapsulation, and backfill) was specified as part of the definition of each scenario as appropriate for the facility type and host rock. Having defined four disposal concepts and their variants, all relevant FEPs were identified that could significantly affect the performance of i-graphite as a disposal wasteform, and the potential interactions between these FEPs were established.

A conceptual contaminant transport model was developed, which was then translated into the GoldSim computational model, with a separate model being created for each of the four scenarios. Through collaboration with CARBOWASTE members, the model parameters were populated with contemporaneous data covering all relevant aspects of the wasteform and repository system.

Performance of scenarios was assessed in terms of peak activity fluxes (Bq/year) across the geosphere / biosphere interface for C-14 and Cl-36; the key-risk radionuclides found within graphite wastes. Gaseous releases were not directly assessed, but were considered as a series of side calculations to determine the potential proportions of organic and inorganic forms of C-14 bearing gases.

The analyses have demonstrated that it should be possible to safely dispose of irradiated graphite wastes in isolation (i.e. in vaults containing only packages of graphite wastes) in a wide range of disposal systems (i.e. combination of disposal concept, EBS and geosphere) and a wide range of host rocks. Assessment calculations show that regulatory guidelines can be satisfied even given conservative assessment assumptions. A broader range of systems might be suitable given less conservative calculation assumptions. One particular issue that potentially requires careful management is the potential impacts associated with disruption of, or large scale intrusion into, an SDF.

It may also be possible to safely dispose of irradiated graphite wastes in the same vaults as other intermediate level wastes (ILW) in a wide range of disposal systems. However, a broader range of processes become important, behaviour becomes more site / design specific and the important scenarios and behaviours may change as the system evolves. This makes it difficult to generically explore the suitability of graphite for geological disposal with other ILW. Specific waste types of concern are those that give rise to bulk gas generation (i.e. metals, organics, strongly irradiating wastes) and that might lead to incorporation of C-14 in methane gas (i.e. organics), and therefore increase the potential for generation and transport of C-14 labelled gases. If transport of C-14 in gas is of concern for segregated graphite waste packages, e.g. potentially in a fractured host rock, it is likely that further performance benefits would be obtained from the disposal of graphite in concrete containers rather than steel containers, thereby reducing bulk gas generation to a very low level. Therefore, although it may not be necessary in all cases, there are advantages to disposing graphite wastes in isolation compared with co-disposal in the same vaults as other ILW.

It is considered that sufficient understanding of i-graphite has now been gained to conclude with confidence, on the basis of work undertaken within CARBOWASTE, that graphite waste can be safely disposed in a wide range of disposal systems. However, in order to prove a safety case for any individual disposal facility, site-specific studies would be required.

8 Selection of Graphite Waste Management Options

The CARBOWASTE project has considered the technical and engineering design aspects of a range of waste management approaches to i-graphite. The next step was to develop a method for assessing the relative merit of the options that have been defined as part of the work. Such an assessment has been carried out to aid decision making, by providing a link between the underpinning science carried out as part of the project and the implementation of i-graphite management options. An assessment of waste management options must:

- address the complete life cycle: in reactor storage, conditioning, retrieval and treatment to final disposal;
- provide a "cradle to grave" approach from in-situ graphite to final solution; and
- provide a "toolbox" approach capable of application to different situations and member states.

Through ongoing interaction between CARBOWASTE work packages, consensus was achieved on twenty four potential options for the management of i-graphite (Mierzewska, 2011), which are provided in Table 1. Further detail on each of the options is provided in Wareing *et al* (2013). The options address the complete life cycle: in-reactor storage, conditioning, retrieval and treatment to final disposal.

Table 1 List of twenty four options considered for assessment

Option No.	Description
1	Encapsulation and deep repository
2	Size reduce graphite for minimised waste package volume; local immobilisation
3	Minimum processing
4	Deferred start with remote retrieval
5	Deferred start with manual retrieval
6	Minimum processing with deferred start
7	Alternative retrieval and graphite form in package
8	Alternative retrieval and repository
9	Interim storage and repository
10	Alternative retrieval, encapsulation and intermediate storage
11	In-situ treatment and near-surface repository
12	Ex-situ treatment and near surface repository
13	Gasification and isotopic dilution with conventional fossil fuel CO_2
14	Gasification and isotopic dilution with conventional fossil fuel CO_2 as a result of sequestration
15	Gasification and isotopic dilution by dispersal as CO_3 in the sea
16	C-14 re-use
17	C-14 re-use with no isotope separation
18	Graphite re-use for nuclear application only
19	In-situ entombment
20	Waste volume reduction and emission to atmosphere
21	Make use of graphite as inert filler, removing the need for some encapsulation
22	Immobilise in medium impermeable to C-14
23	Chemically bind C-14
24	Interim storage of raw waste and repository

The subsequent assessments of these options provided a "cradle to grave" approach from in-situ graphite to final solution. Quantitative assessments were carried out in terms of the impacts of each option on a set of criteria and sub-criteria (Ross and Jarvis, 2009), agreed by representatives from the CARBOWASTE project, provided in Figure 7.

Seven criteria are defined, based on three high level objectives (Table 2):

Table 2 High level objectives for assessment of i-graphite management options

Objective 1: Environmental and Safety	Criterion 1: Environment and Public Safety
	Criterion 2: Worker Safety
	Criterion 3: Security
Objective 2: Economic	Criterion 4: Economic Cost and Benefit
	Criterion 5: Technology Predictability
Objective 3: Social	Criterion 6: Stability of Employment
	Criterion 7: Burden on Future Generations

Environment and Public Safety
This criterion considers the potential for an option to have impacts on the environment. Since members of the public form part of this environment, impacts to them are also included here. Workers employed on the project to deliver the option are subject to additional hazards and so are considered separately in the Worker Safety criterion.

Regulated discharges to the environment are considered as part of this criterion. Releases may be radiological or non-radiological (e.g. toxic materials), or a mixture of both. Use of natural resources and impacts of operations on ecosystems are also considered here.

Worker Safety
The Environment and Public Safety criterion considers public safety; however the workforce will be exposed to risks over and above those borne by the public since they are working on a decommissioning site. It is therefore important that worker safety is considered to select preferred strategy options. Both radiological (dose) and non-radiological (e.g. falls, asphyxiation) impacts are considered.

Security
This criterion considers the protection afforded against deliberate, malicious actions. Two aspects are identified: protection against misappropriation of materials and vulnerability of materials and buildings to malicious, purposeful attacks. The criterion also considers any safeguards necessary to support nuclear non-proliferation.

Economic Costs and Benefits
Economic factors include, at their simplest, the cost of delivering the project. This cost will be assessed over all project phases and will include the costs of research and development, design, construction, operation and decommissioning of any facility. Costs include the processing and treatment of wastes and secondary wastes formed as part of operations. Economics can also consider the benefits of potential spin-off work. Since timescales can be very long for the complete project (from the *in-situ* state to the disposed state), an appropriate discount rate must be selected and applied.

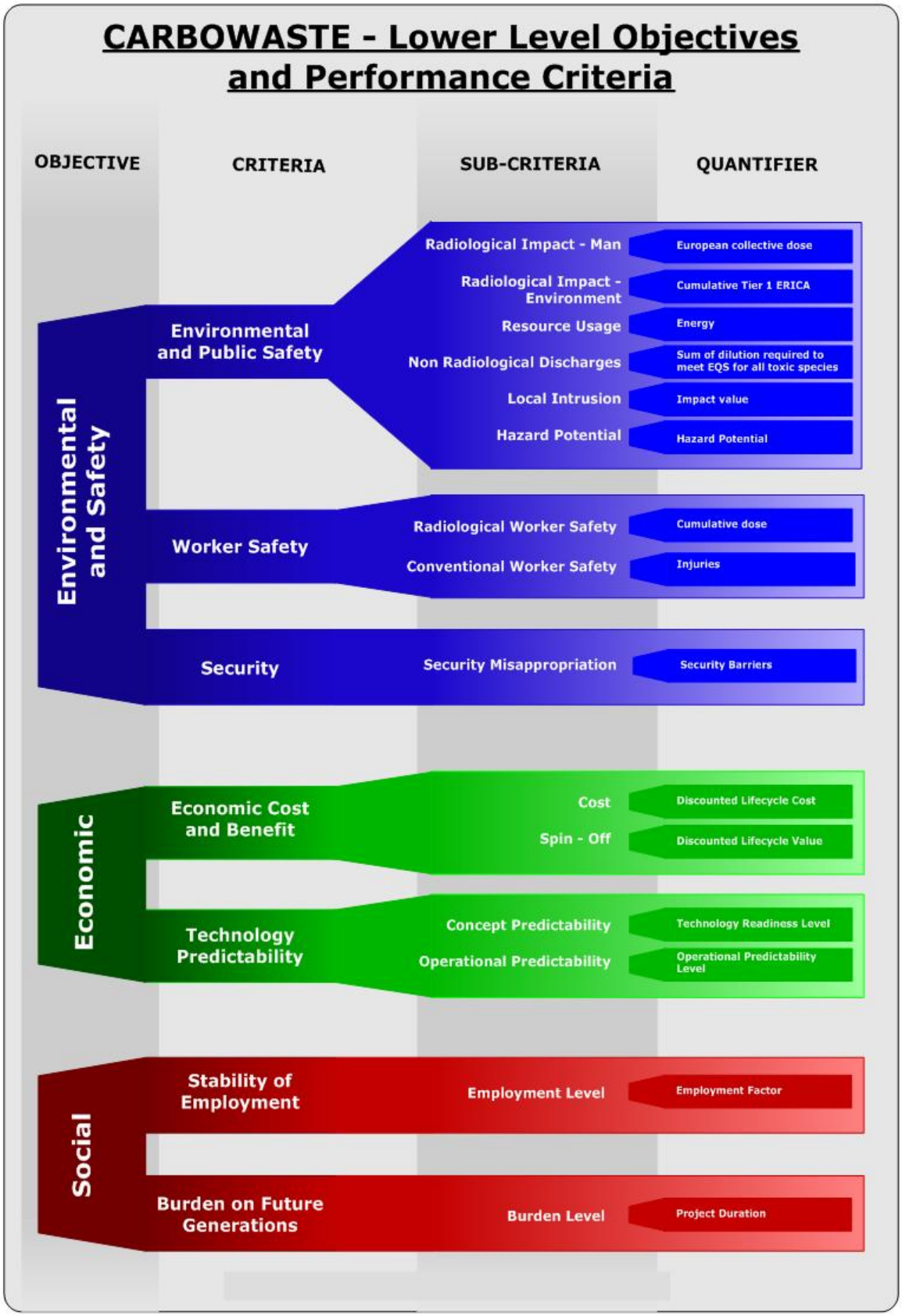

Figure 7 Criteria Summary Diagram

Technology Predictability
Technology selection will have impacts in several criteria. Emissions and effluents will influence the Environment and Public Safety criterion, the nature of the technology (e.g. hands-on vs. remote handling) will affect the Worker Safety criterion, capital and operating costs will influence the Economic Costs and Benefits criterion. Thus, most performance measures are reflected elsewhere. However, there is uncertainty associated with the feed materials and potentially equipment performance, when it is deployed, and this uncertainty results in the need for this criterion.

This criterion considers both the design uncertainty associated with untested equipment, and the flexibility and robustness of the equipment to variations in the feed and operating conditions.

Stability of Employment
Nuclear power stations are often located in remote regions, and are frequently a major local employer. Dramatic swings in employment can therefore have significant local impacts. Closing facilities can result in high unemployment, while construction projects can stretch the local infrastructure, making life unpleasant for local residents. Managed change in employment levels allows the community time to adjust to change.

Burden on Future Generations
A problem with the criteria above is that continual delay might appear to be a preferred option: radioactivity decays to lower levels, costs are depreciated and arisings of waste materials are deferred and potentially reduced. However, staff experienced in the operation of the plant retire and knowledge about the nature of the wastes is lost, buildings decay and there are moral concerns in leaving work for future generations when the benefits of the reactor operation have been experienced by the current generation. These aspects are grouped together and assessed as part of this criterion.

Each of the criteria described above is supported (and assessed quantitatively) by a number of sub-criteria, shown in Figure 7, with detail provided in Ross and Jarvis (2009). The work carried out as part of CARBOWASTE provides the data that enables evaluation of options against these sub-criteria.

Another key criterion to be considered during the assessment of waste management options is that of public acceptance. The assessments carried out for CARBOWASTE have not attempted to quantify the acceptability of options to members of the public, since this is difficult to predict, and is likely to differ considerably across Member States carrying out their own assessments. It is likely that impacts on certain criteria will influence, above others, the acceptability of options to members of the public. Affected communities will include those located close to reactor stations, treatment or storage facilities and the site of any waste repositories that might be constructed, as well as populations as a whole.

For each option, an associated flowsheet was produced, giving an overview of the processes involved, with calculation sheets for each of the stages of the i-graphite process between end points, e.g. in-situ reactor storage, retrieval, treatment, etc. These sheets consider each stage of the process and calculate the associated impact on each sub-criterion. The calculation sheets determine a numerical measure for each sub-criterion. These values have different units, e.g. energy use (GJ) vs. transport (truck journeys), making direct comparison difficult.

A process of MCDA was undertaken in order to compare options like for like. This allows a normalised, unitless, score to be allocated to each option's impact on each sub-criterion. A number of sensitivity cases were examined to determine the effects of various normalised scoring and weighting configurations. Further detail on the process and results of the MCDA assessment can be found in Wareing *et al* (2013) and Abrahamsen & Wareing (2013).

The purpose of the MCDA assessment was to identify and test a process that can be utilised by the CARBOWASTE partner countries. It is not possible to select a preferred option for all countries, since each will have its own specific national strategies, constraints and regulations that will preclude certain options from being viable.

Three case studies were considered, with i-graphite present in:

1. A power reactor;
2. A silo / vault; and
3. A research / experimental reactor.

When assessing all twenty four options (and not removing any based on constraints), Option 19 (*in-situ* entombment) performs best and Option 10 (indefinite storage) performs worst for Case Study 1 (power reactor). The entombment concept, however, in which a reactor is entombed and fully decommissioned *in-situ,* with no further intervention, may not be technically achievable.

The principal safety benefits to be gained from *in-situ* entombment are from significantly reduced radioactive waste handling activities. This would be offset by the need to remove higher activity / longer-lived nuclides to an acceptable level to avoid the need for long term institutional control. The *in-situ* decommissioning approach has been implemented on a number of structures at the US National Labs at Hanford, Idaho and Savannah River sites. The prototype Arbeitsgemeinschaft Versuchsreaktor (AVR) reactor at Jülich has undergone a process of temporary concrete entombment, followed by transport to a storage facility, with the long term plan of dismantlement and *ex-situ* decommissioning. Temporary entombment structures have been erected around acutely damaged reactors, such as those at Chernobyl and Fukushima, but the approach of permanent entombment has not been applied in practice to power reactors. It is almost certain that ongoing maintenance and monitoring of a site decommissioned in this manner would be required for a prolonged period.

The suitability of the approach of entombment will depend strongly on whether there are drivers for the de-licensing of the site. If the long term plan for the site is for it to remain licensed (such as a number of the US National Lab sites), this may be an appropriate option. However, reactors located on sites for which there are drivers for early decommissioning and de-licensing, such an approach would be unsuitable. A more detailed assessment of the entombment concept is provided in Abrahamsen & Wareing (2013).

Options that avoid the use of a deep geological repository perform well in this assessment due to the avoidance of the significant resource usage and economic costs associated with repository construction. The scaled allocation of these impacts to i-graphite needs to be considered alongside member states' national strategies, however. Options that include the use of a deep geological repository perform moderately well in this assessment due to the improved radiological discharges, hazard potential and security impacts balanced against the negative impacts of repository

construction. The worst scoring options are those which consider large, repeated construction activities, such as many treatment facilities or indefinite storage.

Different weighting systems were applied to examine the effects of varying the impact of each criterion in determining the overall weighted score. It was found that, for the twenty four options considered, the different weighting allocations had little effect in determining the relative rankings.

A qualitative assessment was undertaken for Case Studies 2 and 3 (i-graphite in a vault/silo, and a research reactor). Each of the twenty four options was examined to identify particular stages that could not be applied, or would require significant modification to apply, to Case Study 2 or Case Study 3. It was noted that, other than the early process stages in all options not being applicable to graphite in a vault, the majority of options remain appropriate for each of the three Case Studies, although specific practicalities for application may vary slightly.

The assessment process carried out for i-graphite management options has shown that a linear additive method of MCDA is suitable for assessing CARBOWASTE options. However, it is not possible to state here which option is best for any individual member state. Individual member states can use the tools and processes described to determine their own best option(s) by applying their own scores, weightings and constraints. The assessment tool provides supporting arguments in a wider process for the identification of preferred options for the management of i-graphite that will need to take into context many more factors that cannot be represented quantitatively, such as national strategies, regulatory approval or public acceptability.

9 Conclusions

The principal investigations in CARBOWASTE have ensured that the best-available and most environmentally acceptable technologies have been identified for characterisation, retrieval, treatment, reuse/recycling and disposal of i-graphite. This report has presented the assimilation of key findings of CARBOWASTE as an integrated approach for the management of i-graphite wastes.

The following conclusions have been identified in the development of an integrated waste management approach for i-graphite:

1. Characterisation – Graphite is a complex inhomogeneous material and generalisations about its behaviour during irradiation and its final condition should be avoided. The source of material (particularly the reactor type) and its irradiation history are key factors which will determine the ultimate condition of the material, i.e. the quantity and location of radionuclides within the matrix, and the options for its management. In the context of radionuclide inventories, analytical methods need to be harmonised and extensive sampling is necessary to achieve successful characterisation.

2. Retrieval and segregation – Methods for the dismantlement of graphite cores include individual block removal as well as more destructive, excavation-type processes. A period of in-reactor storage, i.e. a delay to retrievals, could reduce doses to operators by allowing the radioactive decay of shorter-lived radionuclides (e.g. tritium and cobalt-60). Doses will also depend on the level of automated versus manual retrieval techniques employed. However, doses incurred throughout the entire graphite management process also need to be considered. An underwater retrieval process could reduce doses to operators and help with dust management, but with the unavoidable generation of a new, aqueous waste stream that would require management. Retrieval has already successfully been achieved at GLEEP and WAGR in the UK and at Fort St Vrain and Brookhaven in the US. Segregation may be an option either during the retrieval process or during packaging after retrieval to separate different waste forms for treatment or disposal.

3. Treatment – Depending upon the radionuclide content of the specific graphite, partial decontamination by heat treatment and oxidation offer credible options. Aqueous chemical treatment requires harsh environments but other chemical treatments such as steam reformation with off-gases incorporated in future carbon sequestration programmes may be an option. Intercalation processes using organic solvents assisted by ultrasound resulting in a dispersion of graphite in a workable medium may also be an option. However, decontamination of graphite by such processes generates secondary waste for which a disposal solution will be required.

4. Packaging and disposal – A range of waste package types and encapsulants are available for the retardation of radionuclide releases at disposal sites. The performance of waste packages has been investigated for a range of generic case geologies (evaporites, fractured hard rock and clay rock), but specific assessments will be necessary when final disposal sites have been selected

It is considered that sufficient understanding of i-graphite has now been gained to conclude with confidence, on the basis of work undertaken within CARBOWASTE, that graphite waste can be safely disposed in a wide range of disposal systems. However, in order to prove a safety case for any individual disposal facility, site-specific studies would be required.

5. Recycle and reuse – The feasibility of recycle and reuse of irradiated graphite has been highlighted, although there is unlikely to be a sufficient market for significant quantities of irradiated graphite. No practical and economical options for isotope separation have been identified.

6. Integrated graphite waste management – A process for the evaluation and comparison of graphite waste management options for irradiated graphite has been developed with multi-criteria decision analysis. Twenty four waste management options have been assessed to identify and test the process that can be utilised by the CARBOWASTE partner countries. Preferred options for different countries will vary depending upon specific national strategies, constraints and regulations.

7. Project outcomes – The collaboration on harmonising methods for performing leaching experiments and pooling data has provided a more complete and rational understanding of radionuclide mobility. The project has created a European-wide collaboration on this specialist topic, which has now expanded to global cooperation through the International Atomic Energy Agency (IAEA). The work undertaken has achieved a better understanding of graphite waste management options through combining results and findings from different groups and has started to make a practical difference to national plans and actions in managing graphite. CARBOWASTE has been an excellent example of knowledge transfer to the “next generation”.

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11 Glossary

AGR	Advanced Gas-Cooled Reactor (UK)
AM	Atom Mirny Reactor (Russia)
AMB	Atom Mirny B Reactor (Russia)
AVR	Experimental Reactor (Germany)
CASTOR	Cask for Storage and Transport of Nuclear Material (Germany)
CEA	Commissariat à l'énergie atomique (France)
CPS	Control and Protection System
DIDO	Enriched uranium reactor with heavy water coolant/moderator (UK)
DOE	Department of Energy (US)
EBS	Engineered Barrier System
EDF	Électricité de France
EGP-6	Light water-cooled graphite moderated-reactor (Russia)
FEP	Features, Events and Processes
GDF	Geological Disposal Facility
GLEEP	Graphite Low Energy Experimental Pile (UK)
HTR	High Temperature Reactor
HTTR	High Temperature Test Reactor
IAEA	International Atomic Energy Agency
ILW	Intermediate Level Waste
INPP	Ignalina Nuclear Power Plant (Lithuania)
JEN-1	Experimental Reactor (Spain)
LLW	Low Level Waste
MCDA	Multi-Attribute Decision Analysis
NPP	Nuclear Power Plant
NRC	Nuclear Regulatory Commission
PBMR	Pebble Bed Modular Reactor (South Africa)
RATA	State Enterprise Radioactive Waste Management Agency (Lithuania)
RBMK	High-power channel-type reactor (Russia)
THTR	Thorium High Temperature Reactor (Germany)
UNGG	Uranium Naturel Graphite Gaz reactor (France)
WAGR	Windscale Advanced Gas-cooled Reactor (UK)
WP	Work Package (CARBOWASTE)