Nuclear Engineering and Technology 49 (2017) 1010–1018

Contents lists available at ScienceDirect

Nuclear Engineering and Technology

journal homepage: www.elsevier.com/locate/net

Original Article

Development of integrated waste management options for irradiated graphite

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ARTICLE INFO

Article history:
Received 19 December 2016
Accepted 21 March 2017
Available online 27 March 2017

Keywords:
Decision Framework
Integrated Waste Management
Irradiated Graphite
Nuclear Reactor Decommissioning
Radioactive Waste Management

ABSTRACT

The European Treatment and Disposal of Irradiated Graphite and other Carbonaceous Waste project sought to develop best practices in the retrieval, treatment, and disposal of irradiated graphite including other irradiated carbonaceous waste such as structural material made of graphite, nongraphitized carbon bricks, and fuel coatings. Emphasis was given on legacy irradiated graphite, as this represents a significant inventory in respective national waste management programs. This paper provides an overview of the characteristics of graphite irradiated during its use, primarily as a moderator material, within nuclear reactors. It describes the potential techniques applicable to the retrieval, treatment, recycling/reuse, and disposal of these graphite wastes. Considering the lifecycle of nuclear graphite, from manufacture to final disposal, a number of waste management options have been developed. These options consider the techniques and technologies required to address each stage of the lifecycle, such as segregation, treatment, recycle, and ultimate disposal in a radioactive waste repository, providing a toolbox to aid operators and regulators to determine the most appropriate management strategy. It is noted that national waste management programs currently have, or are in the process of developing, respective approaches to irradiated graphite management. The output of the Treatment and Disposal of Irradiated Graphite and other Carbonaceous Waste project is intended to aid these considerations, rather than dictate them.

1. Introduction

The use of graphite in nuclear reactors worldwide as a moderator, reflector, or operational material results in an accumulation of radioactivity by neutron activation both of the constituent elements of graphite and of impurities, as well as potential contamination of its surface. This irradiated graphite (i-graphite) presents a major waste management challenge due to the presence of long-lived radionuclide species such as ^{14}C and ^{36}Cl, together with shorter-lived species including ^{3}H and ^{60}Co, and small quantities of fission products and actinides.

Over 250,000 tons of i-graphite have been accumulated worldwide [1], ranging from countries with a fleet of multiple graphite-moderated power reactors (e.g., UK and France), prototypes, and production reactors to those with a single experimental reactor. Irradiated and contaminated graphite from reactor moderators and reflectors or thermal columns represent the greatest volume of these waste materials. Currently, the majority of this i-graphite is held either *in situ* within reactors or in vault/silo storage. Furthermore, Smith and Bredell [2] have identified the potential large volumes of i-graphite associated with the potential future use of pebble bed modular reactors.

There are various options that could be adopted as waste management solutions for i-graphite, and many of these have been investigated during the recent European Commission project "Treatment and Disposal of Irradiated Graphite and other Carbonaceous Waste (CARBOWASTE)" under the seventh European Atomic Energy Community Framework Programme [3]. The project was designed to develop best practices in the retrieval, treatment, and disposal of i-graphite and to deliver an integrated waste

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http://dx.doi.org/10.1016/j.net.2017.03.001
1738-5733/

management approach suitable for application by different countries and sites, each with their own particular conditions to meet (e.g., a specific disposal end point or regulatory requirements). However, the purpose was not to dictate a national waste management strategy in relation to i-graphite. The CARBOWASTE project brought together organizations and stakeholders from the nuclear industry and scientific research establishments from European countries, as well as other international partners, to share knowledge and develop methodologies for i-graphite management [4].

Fig. 1 provides a schematic diagram of an example of i-graphite lifecycle, showing the principal stages from graphite manufacture to final disposal. During manufacture, impurities become associated with the graphite matrix, which, along with naturally occurring carbon isotopes, leads to the generation of a range of radionuclides within the graphite matrix during reactor operation (see Section 2.1.1).

Following the shutdown of a reactor, the radioactive inventory within the i-graphite will decrease with time, due to radioactive decay. Following a period of in-reactor storage, the point at which the i-graphite is retrieved will influence the radiological hazard posed by the material, since some of the radionuclides present are relatively short lived. While the radioactivity associated with i-graphite cannot be destroyed, methods of treatment or conditioning can be used to convert it into alternative, more manageable physical and chemical forms. A decontamination process may reduce the radioactivity associated with the bulk graphite matrix, but, in doing so, will generate a secondary waste stream that must also be appropriately managed. It may be possible to recycle or reuse i-graphite materials, e.g., the use of decontaminated graphite in other industrial processes. However, due to the long half-lives of a number of the radionuclides present, e.g., ^{36}Cl (308,000 years), it is likely that some material will require a disposal method that isolates it from the environment for an extremely long period, e.g., within a geological or engineered (e.g., surface) disposal facility.

Identification of potential options for the management of i-graphite that address each stage of the i-graphite lifecycle needs to account for the specific physical, chemical, and radiological characteristics and behavior of the material. These factors will influence the feasibility and performance of processes and techniques that could be implemented at each stage of the lifecycle.

The objective of this paper is to provide an overview of the characteristics of graphite that has been irradiated via its use, primarily as a moderator material, within nuclear reactors. This paper goes on to describe the potential techniques applicable to the retrieval, treatment, recycling/reuse, and disposal of these graphite wastes. The paper then sets out a number of waste management options that have been developed through consideration of the lifecycle of nuclear graphite, from manufacture to final disposal. These options consider the techniques and technologies required to address each stage of the lifecycle, such as segregation, treatment, recycle, and ultimate disposal in a radioactive waste repository. These options are presented as a toolbox of technologies, together with a proposed methodology and framework of objectives and criteria, to aid the selection of the most appropriate solution for a specific situation.

2. Characteristics of i-graphite

2.1. Background

The behavior of graphite during irradiation and its final condition as a waste material will depend on the range of raw materials used in the manufacturing process; its physical, mechanical, and thermal properties; and its role in the reactor (e.g., moderator/shield/reflector/fuel assembly), which will determine its exposure environment. As such, there is no generic radionuclide inventory of i-graphite. While radionuclide inventories can be estimated using activation modeling [5,6], these will only be accurate if the quantities of impurities are well characterized. There also needs to be a certain amount of direct measurement of representative material to understand more fully the distribution of radioactive species, and the total inventory, within a particular source of i-graphite.

Knowledge of radionuclide precursors present in i-graphite (e.g., isotopes of chlorine, oxygen, and nitrogen) will inform the potential methods for waste treatment and the potential release mechanisms in a disposal facility, in the event that some or all of the i-graphite is disposed of in this way. The location of radioisotopes within i-graphite will influence their mobility, while their distribution may provide the potential for segregation of the i-graphite material (e.g., into streams of different radioactivities) during or following its retrieval.

2.1.1. Origin and nature of radioactivity in i-graphite

There are three main sources for the radioactivity associated with i-graphite. (1) Activation (via fast neutron capture) of atoms within the graphite structure, e.g., naturally occurring ^{13}C that is present within the graphite lattice structure, as well as impurities introduced during the manufacture of graphite, such as chlorine, nitrogen, cobalt, and lithium isotopes. These processes lead to the generation of mainly ^{14}C (half-life 5,760 years), ^{36}Cl (half-life 308,000 years), ^{60}Co (half-life 5.3 years), and ^{3}H (tritium, half-life 12.3 years) radioisotopes. (2) Activation of atoms deposited on the graphite surface during reactor operation. These generally arise from the reactor coolant and can include isotopes of nitrogen and oxygen, leading mainly to the generation of ^{14}C. (3) Contamination of the i-graphite surface during reactor operations. These deposited species can include radionuclides arising within the reactor circuit or activation products circulated in the coolant. Quantities of fission products, uranium, and transuranic elements may contaminate the i-graphite as a result of fuel failures during operation of the reactor or from traces of uranium carried into the core on fuel-element surfaces. The half-lives of these species can vary from seconds to hundreds of thousands of years.

Neglecting gross contamination, ^{14}C, ^{36}Cl, ^{3}H, and ^{60}Co are the most significant radioisotopes for determining an integrated waste management approach for i-graphite. The short half-lives of ^{60}Co and ^{3}H mean that these species are most significant in the years immediately following reactor shutdown. In cases where retrieval and treatment are delayed for a period of several decades following reactor shutdown, ^{60}Co and ^{3}H activity will largely have decayed away to low levels.

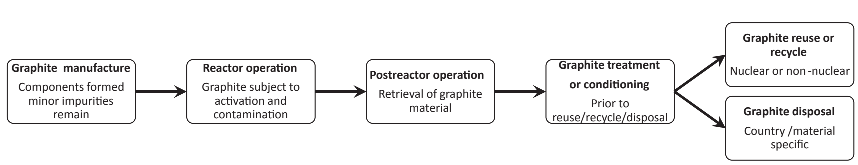


Fig. 1. Schematic of i-graphite lifecycle.

2.1.2. Location of radioactivity within i-graphite

The origin of the impurities or precursors will determine the location of the radionuclides. An extrinsic origin, e.g., from reactor coolant, will give rise to surface-bound radionuclides, whereas an intrinsic origin, e.g., from activation, will result in the radionuclide being either "trapped" interstitially or intercalated inside the graphite structure (Fig. 2). The activation product tritium (^{3}H), however, can readily diffuse through the graphite matrix to pore surfaces.

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 that are located within the graphite structure will only be removed through the application of more destructive techniques. Thus, characterization 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 treatment regime that may be required for their removal. For example, ^{14}C bound within the graphite matrix may not be readily removed via treatment methods. An additional point to consider is that such strongly bound radioactivity would be expected to be released more slowly from i-graphite following disposal, and its prior removal via treatment might not be deemed necessary.

2.1.3. Additional effects of reactor operations

In addition to the generation of radioactivity within, and on the surface of, i-graphite, irradiation within a reactor leads to other changes in the physical and chemical properties of the graphite material. These could have significant implications for the selection of retrieval techniques, as well as the options available for packaging and any treatment or recycle approaches.

2.1.4. Irradiation damage

When a fast neutron collides with a carbon nucleus, while passing through nuclear graphite, atoms are displaced from their lattice positions and interjected into the immediate surroundings, leading to lattice point defects. This behavior can result in bulk dimensional change as well as affect the mechanical properties of the bulk material.

One further 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 can be, if deemed significant, offset by thermal annealing, which is the process of heating the graphite beyond its normal operating temperature within the reactor in order to release the accumulated energy in a controlled manner. Modern reactor operational conditions mean that the presence of Wigner energy within i-graphite is not expected to be a significant issue.

2.1.5. Radiation chemistry effects

In CO_2-cooled reactors, radiolytic oxidation will occur, in which CO_2 gas reacts with ionizing radiation to produce oxidizing species. These can oxidize the graphite surface, resulting in a loss of graphite mass to the gas phase and the release of radioisotopes that were previously fixed within the graphite lattice. Some of this radioactivity will be released to the atmosphere during reactor operation. In the highest flux region of a Magnox reactor, for example, core mass losses from oxidation can be up to ~40% from the virgin state. As well as having a significant effect on the i-graphite inventory due to mass loss, oxidation will lead to degradation of the graphite's hardness, strength, and thermal conductivity. Such effects could have an impact on the options available for retrieval and handling.

Physical, chemical, and radiological characteristics of i-graphite, as described above, can, therefore, have a significant bearing on the waste management processes that are suitable to employ at different stages of the lifecycle. An approach to facilitate the selection of waste management options for i-graphite is described in the following section.

3. Integrated waste management approach

An integrated waste management approach for i-graphite enables a comprehensive analysis of the key stages from in-reactor storage through to final disposal, accounting for economic, safety, environmental, and sociopolitical factors. The approach developed within the CARBOWASTE project constitutes an optioneering study that could be used to inform national waste management approaches, but recognizes that some countries already have approaches in operation or planning. The approach involves the definition of a generic route map for i-graphite, followed by a series of detailed waste management scenarios (options) that are evaluated against specific criteria. This approach is supported and underpinned by information relating to the current strategies and technologies associated with the management of i-graphite and other radioactive wastes both nationally [7] and internationally, together with experimental, modeling, and other analyses performed within the CARBOWASTE project. The generic integrated waste management methodology is applicable to other radioactive waste management challenges, beyond i-graphite.

3.1. The i-graphite route map

The i-graphite route map identifies the key stages and issues that should be considered to enable an informed i-graphite waste management option to be selected [8,9]. Based on the generic lifecycle shown in Fig. 1, the route map presents the key factors that will influence any waste management strategy for i-graphite and the information requirements to enable subsequent evaluation of options. The route map covers the six steps shown in Fig. 3,

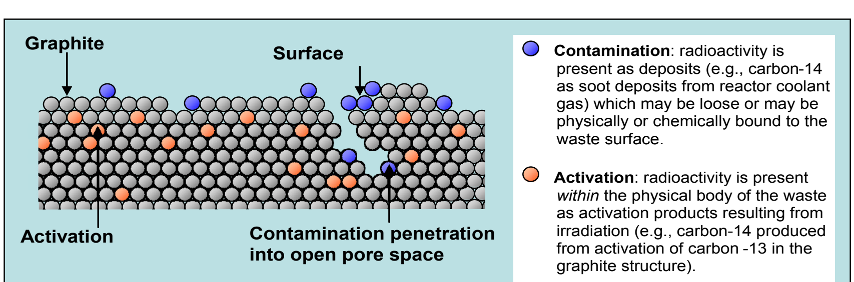


Fig. 2. Schematic molecular cross-section of i-graphite showing typical distribution of contaminants.

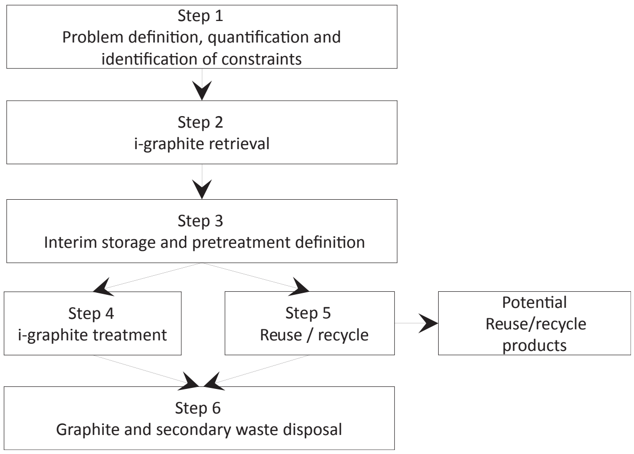


Fig. 3. Overview of the irradiated graphite route map. *Note:* Figure 3 is based on an original roadmap [9] (Copyright © 2012 Elsevier B.V.).

consisting of defining the i-graphite problem (inventory, reactor type, irradiation history, and storage period), followed by consideration of retrieval, interim storage, treatment, reuse/recycle, and disposal. Definition of the disposal end point informs the scope of the upstream steps in the route map. The route map sets out the framework within which waste management options can be defined for subsequent evaluation.

3.1.1. *Retrieval and segregation*

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 [10]. Integration of the graphite fixing and support materials in the core, as well as *in situ* measuring devices, creates a diverse "gangue" material that is associated with the i-graphite material and may need to be separated into different waste streams for treatment or disposal. Associated metallic components may contain a significant inventory of ^{60}Co, as well as other activation products.

Retrieval of i-graphite may take place in air, under water, or potentially in an inert atmosphere to minimize risks from ignition or explosion of graphite dust. Underwater retrieval has been demonstrated during the decommissioning of the Fort St Vrain reactor in Colorado, USA. This technique allows proximity to the workface, with good line of sight, personnel shielding, and the opportunity to use simple manual tooling. Additionally, a significant fraction of ^{36}Cl and other loosely bound contamination would be leached from the i-graphite into the water. This results in a lower radiological inventory for the i-graphite, but has the disadvantage of generating a significant volume of contaminated water that will require separate management.

One option for the retrieval of i-graphite is to dismantle the core by removing the blocks individually. This approach has been undertaken successfully on the prototype Windscale Advanced Gas Reactor using a ball grab mechanism [11]. A process of in-air individual block drill and tap retrieval was used in the decommissioning of the Graphite Low Energy Experimental Pile [12]. Block removal may present difficulties relating to dealing with cracked, broken, or fused blocks in some situations.

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 [13]. This approach involves breaking up the graphite prior to its removal in baskets. Another proposed technique is to break up the graphite *in situ* into small pieces, followed by removal by suspension in air or nitrogen via a vacuum retrieval system.

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 to 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.

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.

3.1.2. *Treatment processes*

Treatment of i-graphite may be undertaken for a variety of reasons: (1) to reduce dose to workers; (2) to reduce volumes of waste for disposal; (3) to achieve the radiological requirements for disposal; and (4) to facilitate recycle or reuse of isotopes or graphite.

Wallbridge et al. [14] identified, through lifecycle analysis, that the majority of environmental impacts from decommissioning a power station are directly related to the amount of waste that needs to be packaged and stored. Decontamination processes are, therefore, advantageous for removing a substantial proportion of the radionuclide inventory from the primary wasteform. They also affect the form and properties of the end product, and define the form and nature of the waste streams produced.

It is recognized that the requirement, or otherwise, for i-graphite treatment varies from country to country, and some nations may determine that treatment is not required.

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 disposal facility. Therefore, i-graphite to be routed to a near-surface disposal facility may require more significant decontamination or treatment prior to packaging and disposal. Conversely, i-graphite waste destined for a geological disposal facility may not require any treatment.

Treatment processes can be loosely classified as thermal or chemical, although it is recognized that some processes can cross over these two groups (e.g., steam reformation), often combining elements of the two. Thermal treatments involve heating the graphite in an inert atmosphere to a sufficiently high temperature such that the adsorbed radioisotopes become mobile. 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). Steam reformation transforms graphite fragments by high-temperature interaction with steam into two combustible gases (hydrogen and carbon monoxide). After oxidation and transformation into CO_2 and water, the gas is released to the atmosphere through a high-efficiency particulate air filter [1].

The aerial release of some of the more mobile/volatile radionuclides will need to be assessed for acceptability. Thermal treatment processes and the effect of thermal processes on ^{14}C, ^{3}H, and ^{36}Cl have been investigated by various researchers, including Vulpius et al. [15], Le Guillou et al. [16], Blondel et al. [17], and Vaudey et al. [18].

Chemical treatment processes can decontaminate graphite by selectively removing the surface layer and destroying the binder material. It should be noted that while decontamination methods can reduce the radioactive inventory of the graphite material, the additional radioactive waste streams generated as part of the process must also be managed properly.

3.1.3. *Reuse/recycle*

A number of potential approaches exist for the recycling of i-graphite materials. These include the separation and enrichment (concentrating) of ^{14}C for use in the medical and chemical industries. This would require an efficient means of separating the ^{14}C from the graphite, and the resulting product would need to have the correct characteristics of chemical form, isotopic purity, and quantity, for supply to the market.

Recycling of material (either graphite or separated isotopes) will depend heavily on demand and cost in order to be economically viable. The potential processes for recycle require further development, and studies as part of the CARBOWASTE project concluded that a large-scale application of these is not *currently* economically viable.

3.1.4. *Disposal*

Options for the ultimate disposal of i-graphite as a wasteform are influenced by many factors, including radioactive inventory, volume, wasteform, and timing, and, importantly, by the availability of a suitable disposal facility with its own associated waste acceptance criteria. The aims of any pretreatment and conditioning of waste must be consistent with the disposal requirements. Local infrastructure, national policy, and regulation relating to disposal vary from country to country, and these have a major influence on the options that need to be considered and the output requirements of the retrieval/segregation and treatment technologies employed.

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 that any radionuclide transfer back to the environment is radiologically insignificant and meets regulatory criteria. Options for disposal include surface disposal facilities, deep geological disposal facilities (e.g., 1 km depth), or facilities at some intermediate depth (e.g., 100 m depth).

In order to assess whether i-graphite can be disposed of as waste with or without further treatment, its behavior under disposal conditions needs to be assessed. Disposal conditions are influenced by the natural geological and hydrogeological environment and by the waste package and other engineered barrier systems. Following degradation of the engineered barrier systems and waste packaging, groundwater may permeate the i-graphite porosity, although this will be heavily dependent on the geology of the repository host rock. Groundwater ingress will lead to radionuclides leaching from the i-graphite, and the rate of this leaching will determine the extent of long-term release of radionuclides from the waste material. Radionuclides ^{14}C and ^{36}Cl are of particular interest to repository performance due to their long half-lives. The release rates and migration behavior of these two isotopes will be significantly different due to the intrinsic association of a fraction of ^{14}C within the graphite matrix and the different chemical behavior of these elements following release.

Fig. 4. Option evaluation process (based on the work of Banford et al [22]).

Table 1
Objectives, criteria, and subcriteria for evaluation of waste management options.

Objective	Criteria	Subcriteria
Environment & safety	Environmental & public safety	Radiological impact—humans
		Radiological impact—environment
		Resource usage
		Nonradiological discharges
		Local intrusion
		Hazard potential
	Worker safety	Radiological worker safety
		Conventional worker safety
	Security	Security misappropriation
Economic	Economic cost & benefit	Cost
		Spin-off
	Technology predictability	Concept predictability
		Operational predictability
Social	Stability of employment	Employment level
	Burden on future generations	Burden level

Table 2
Potential i-graphite inventories, strategic goals, and technologies.

Potential i-graphite feed inventories
- Vault/silo graphite—both pure & mixed (e.g., the Vandellos silos, Spain)
- Power reactor core graphite—both reflector & moderator (e.g., as from the Uranium Naturel Graphite Gaz reactors in France)
- Fuel pebbles (generation III/IV fuel form)
- Test reactor graphite [e.g., the heavy-water material test reactor (DIDO) in Germany]
- Cemented graphite—both in core & *ex situ*
- Heavily contaminated graphite—the level of contamination may have an impact on the preferred management strategy
- Decontaminated graphite—graphite that has already been cleaned but may still need further processing, such as repacking
- Nongraphite carbonaceous waste (e.g., nongraphitized carbon bricks)

Potential strategic goals & end states for managing i-graphite
- Cleaned ^{12}C for reuse
- Recover ^{14}C for reuse
- Recycle unclean graphite (reuse in nuclear applications, e.g., electrodes, crucibles)
- Disposal in a deep repository (either a dedicated repository for graphite wastes or codisposal with other waste types)
- Disposal in an intermediate-depth repository (at around 200 m depth)
- Disposal in a near-surface repository
- Codisposal by mixing with grout
- Free release
- Gasification, incineration, & dispersal
- Sequestration
- Entombment (*in situ* immobilization)
- Conversion to carbonate & disperse
- Indefinite storage (either in a reactor or in a store)

Potential operations & technologies
- Characterization
- Bulk block retrieval, both manual & remote, e.g., drill & tap, ball grab, vacuum lift
- Block retrieval under water, in order to provide shielding & reduce dose to operators
- Retrieval as particulate, in air or under water, e.g., nibble & vacuum
- Segregation
- *In situ* treatment, e.g., leaching, chemical treatment, biological treatment, heat treatment/roasting
- *Ex situ* treatment, as for *in situ* treatment but with greater scope to optimize the treatment outside of the reactor
- Recycle
  - Isotope separation, to recover ^{14}C or to reduce ^{14}C in a ^{12}C-rich stream
  - Manufacture of carbon black
- Disposal
  - Compaction/size reduction
  - Chemical binding of ^{14}C
  - Impermeable matrix to retain ^{14}C
  - Gasification by reaction with steam
  - Encapsulation, in cementitious grout or other media
  - Reaction with air/oxygen
  - Sequestration
  - Isotopic dilution, to eliminate future risk of ^{14}C exposure
  - Transport
  - Interim storage

Radionuclides released via leaching may then migrate through the engineered barrier systems and groundwater to the surface environment, via processes of advection and diffusion, and subject to retardation. Radionuclides that have migrated from the disposal facility may potentially enter gaseous form, e.g., $^{14}CH_4$ (methane) or $^{14}CO_2$.

The postdisposal behavior of i-graphite waste can be greatly improved by emplacement in suitable waste packages. For example, one current national program 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 a physical and chemical barrier against the migration of radionuclides away from the waste.

Some products, such as silicon carbide, can be specially manufactured to chemically stabilize carbon in a radioactive waste disposal site, or to act as a confinement or packing material for other wastes and thermal management, in a repository environment. The i-graphite could also be transferred into a long-term stable impermeable alternative waste matrix through vitrification, which would close the i-graphite porosity and inhibit the ingress of water [19–21].

Analyses undertaken within the CARBOWASTE project have demonstrated that it should be possible to safely dispose of i-graphite wastes in isolation (i.e., in vaults containing only packages of graphite wastes) in a wide range of disposal systems and a wide range of host rocks. It may also be possible to safely dispose of i-graphite wastes in the same vaults as other intermediate level wastes. However, the interaction between different wastes needs to be considered, and this is highly influenced by site-specific conditions.

3.2. Process for evaluation of waste management options

Fig. 4 summarizes the option evaluation process for i-graphite management. It is recognized that many countries have fully or partially developed approaches that are already determined and will not be starting from this initial stage.

A process of option identification is necessary at the outset in order to generate a set of scenarios (or options) for i-graphite management that can be evaluated. Following option identification, the option screening phase eliminates some options prior to detailed assessment. Options are screened using a set of site/country-specific constraints (e.g., options must meet all appropriate national and international legislations). For CARBOWASTE, the option assessment was based on evaluation via a series of objectives, criteria, and subcriteria for each option, as shown in Table 1. The high-level environment and safety, economic, and social objectives were chosen in line with the "three pillars of sustainability," as identified in the 2005 World Summit [23].

Table 3
List of potential strategic management options for i-graphite.

Option no.	Description
1	Encapsulation & deep repository: graphite is allowed to decay in the reactor core for 25 yr followed by remote retrieval to recover blocks of graphite for on-site encapsulation. The resulting packages are transported to a vault dedicated to graphite within a deep geological repository.
2	Size reduction of graphite for minimized waste package volume; local immobilization: Option 2 differs from Option 1 in that it performs size reduction prior to encapsulation to increase the packing of graphite into boxes.
3	Minimum processing: Option 3 differs from Option 1 in that it does not perform encapsulation of the waste, but only boxes the waste.
4	Deferred start with remote retrieval: Option 4 differs from Option 1 in that it allows an additional 50 yr for cooling in the reactor & then (in common with Option 2) performs size reduction to increase packing of graphite within boxes. This option also uses a deep geological repository where graphite wastes share a vault with other wastes.
5	Deferred start with manual retrieval: Option 5 differs from Option 4 in that it allows manually assisted retrieval to take place rather than assuming fully remote operation.
6	Minimum processing with deferred start: Option 6 differs from Option 3 in that it includes a longer *in situ* storage period & then uses manually assisted retrieval rather than fully remote retrieval.
7	Alternative retrieval & graphite form in package: Option 7 differs from Option 1 in that the graphite material is retrieved as particulate & is finally disposed of to a deep geological repository in which graphite material shares a vault with other material.
8	Alternative retrieval & repository: Option 8 differs from Option 1 in that the graphite material is retrieved underwater, & interim storage is used to provide time for the provision of an intermediate-depth waste repository.
9	Interim storage & repository: Option 9 differs from Option 1 in that interim storage is used to enable time for construction of an intermediate-depth waste repository.
10	Alternative retrieval, encapsulation, & intermediate storage: Option 10 differs from Option 7 in that it allows interim storage of graphite particles prior to encapsulation, & the final destination is a surface store (which requires replacing every 150 yr).
11	*In situ* treatment & near-surface repository: Option 11 differs from Option 1 in that *in situ* heat treatment is used to condition the graphite at the end of operations. Also, a colocated near-surface repository is used in place of a dedicated deep repository.
12	*Ex situ* treatment & near surface repository: Option 12 differs from Option 1 in that *ex situ* heat treatment is used to condition the graphite to remove ^{14}C. Also, a colocated near-surface repository is used in place of a dedicated deep repository.
13	Gasification & isotopic dilution with conventional fossil fuel CO_2: Option 13 differs from Option 1 in that particulate retrieval is used to recover the graphite. Metal components are segregated from the graphite & encapsulated before the graphite is further reduced in size & gasified before isotopic dilution & release. Also, a colocated repository is used in place of a dedicated deep repository because only metal items & ash are now consigned to the repository.
14	Gasification & isotopic dilution with conventional fossil fuel CO_2 as a result of sequestration: Option 14 differs from Option 13 in that it captures the off-gas from the gasification process & sequesters it along with gases from conventional fossil fuel processes.
15	Gasification & isotopic dilution by dispersal as CO_3: Option 15 differs from Option 13 in that it captures the off-gas from the gasification process & discharges it to sea.
16	^{14}C reuse: Option 16 differs from Option 1 in that it selects a portion of the graphite expected to contain high levels of ^{14}C & segregates it. This graphite is roasted to produce a gaseous stream rich in tritium & ^{14}C. The remaining solid material is then routed to encapsulation & repository. The tritium & ^{14}C are then separated with the ^{14}C subjected to further enrichment before reuse. The depleted ^{12}C rich stream is discharged.
17	^{14}C reuse with no isotope separation: Option 17 differs from Option 16 in that it performs no additional ^{14}C enrichment.
18	Graphite reuse for nuclear application only.
19	*In situ* entombment.
20	Waste volume reduction & emission to atmosphere.
21	Making use of graphite as inert filler, removing the need for some encapsulation.
22	Immobilizing in medium impermeable to ^{14}C.
23	Chemically binding ^{14}C.
24	Interim storage of raw waste followed by disposal to a repository.

4. Development of waste management options

The objective of this task was to define a comprehensive set of plausible options that cover the range of i-graphite wastes, facilities, and waste management policies relevant to different European countries. The options encompass both mature and established technologies, as well as technologies that are more novel but have the potential to provide advantages over more established technologies. In this way, the integrated waste management approach provides a "toolbox" of options that is flexible enough to be applied to different situations and countries. The full list of options can be screened using constraints that address the specific context, policies, and regulations of a particular country.

The identification of options was supported by the outputs and findings from the CARBOWASTE project relating to the key processing stages of retrieval and segregation, treatment, recycle/reuse, and disposal. The options were defined during workshops that brought together experts and stakeholders from the nuclear industry, waste management organizations, utilities, graphite manufacturers, research establishments, and universities.

In preparation for option synthesis, three specific aspects were considered that define the context and applicable technologies for the options: the i-graphite inventory, potential strategic objective (end point), and potential unit operations and techniques that can be applied. These are listed in Table 2.

Several categories of i-graphite materials were identified, for which a range of operations were then defined that could be linked and combined to create options that manage the materials to achieve the chosen strategic goal. By linking these operations together in a consistent manner, 24 potential options for the management of i-graphite were developed (Table 3). These encompass a range of potential strategic options for the different waste types and end points. Other combinations of operations are possible and may be appropriate for some graphite waste streams, but these options were not assessed in the CARBOWASTE project. However, this set of options has demonstrated the development of a process that can be adapted and modified by end users as appropriate, e.g., by introducing other options.

Flow diagrams were prepared for each option to illustrate the process stages and facilitate the collection of data to support subsequent analysis. Examples of the flow diagrams are given in Fig. 5.

When applied to a particular i-graphite feed material, data need to be obtained and collated for each option to inform assessment. To assist in determining data requirements for the evaluation of options, a generic "process stage" for i-graphite waste management was developed (Fig. 6). The generic process stage consists of the following. (1) *Feeds:* This includes the graphite, but may also include other items needed to process the graphite, such as reagents, packages, etc., which require transport. (2) *Resources:* This includes items such as power, water, concrete, and steel used within the facility to manage the wastes. Also included are the resources required to construct and decommission facilities built

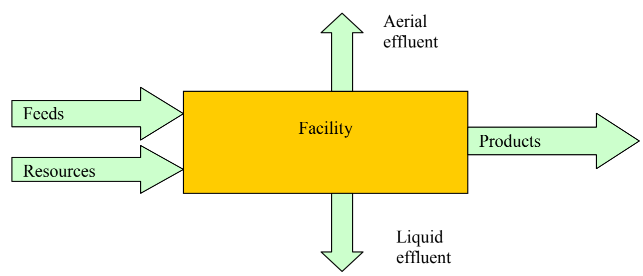


Fig. 6. Generic process stage.

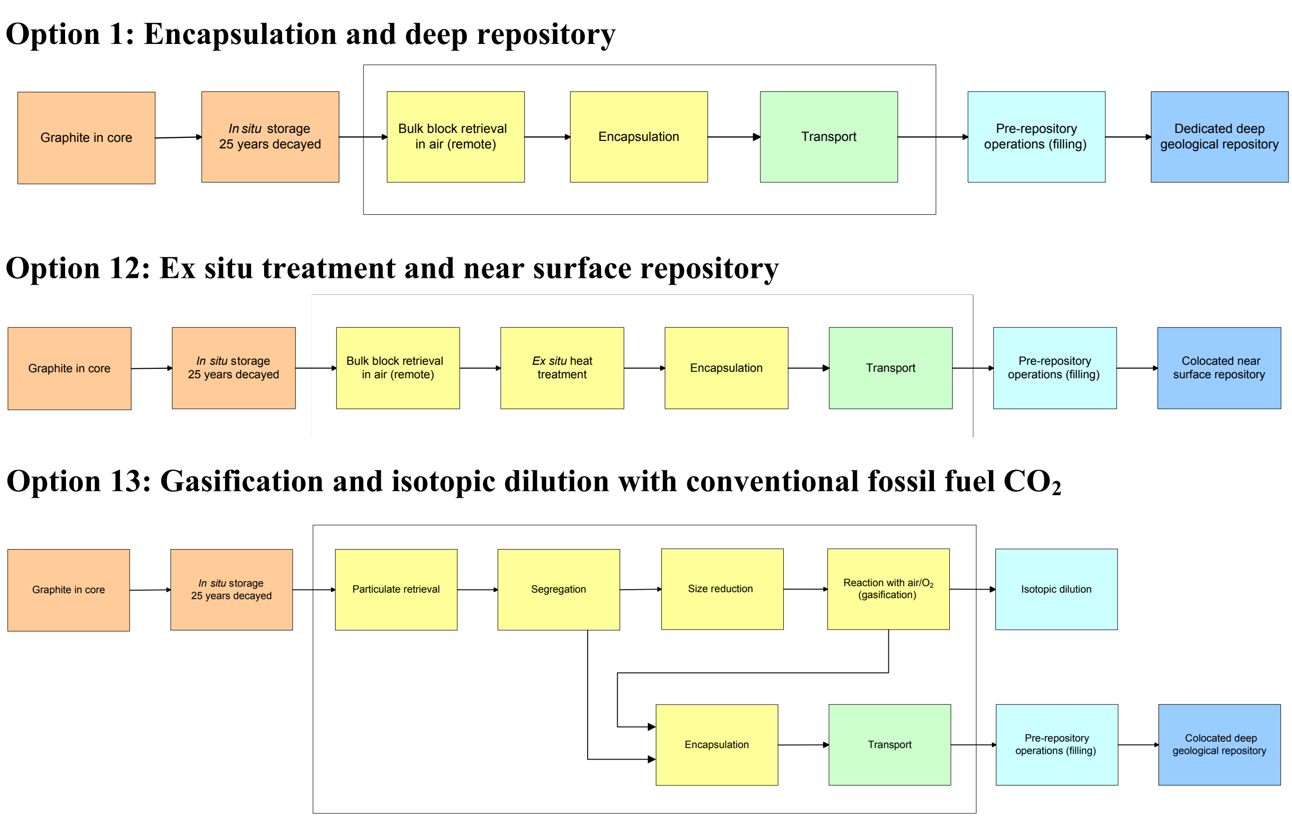
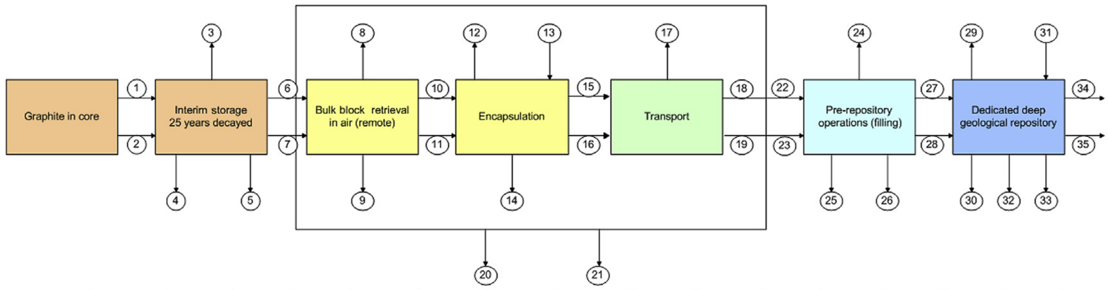


Fig. 5. Flow diagrams for example waste management options.



Stream key																	
Stage 1	Stream no.	1	2	3	4	5											
	Description	Graphite	Steel	Aerial discharge	Radiological decay (graphite)	Radiological decay (steel)											
Stage 2/3	Stream no.	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
	Description	Graphite for retrieval	Steel for retrieval	Aerial discharge	Liquid effluent	Graphite feed for grouting	Steel feed for grouting	Aerial discharge	Grout	Grout bleed effluent	Graphite to transport	Steel to transport	Aerial discharge	Graphite post operations	Steel post operations	Graphite radiological decay	Steel radiological decay
Stage 4	Stream no.	22	23	24	25	26											
	Description	Graphite feed to repository	Steel feed to repository	Aerial discharge	Graphite radiological decay	Steel radiological decay											
Stage 5	Stream no.	27	28	29	30	31	32	33	34	35							
	Description	Graphite post closure feed	Steel post closure feed	Aerial discharge	Liquid discharge to biosphere	Backfill	Graphite radiological decay	Steel radiological decay	Graphite remaining at end of assessment	Steel remaining at end of assessment							

Fig. 7. Input/output data points for example waste management option.

specifically for processing i-graphite. In the event that a facility is shared with other waste streams, a proportion of the resources used in construction/decommissioning the facility are relevant to the evaluation. (3) *Facility:* In addition to the resources used in constructing a facility, other details, such as workforce, technology used, and cost, are required across the lifetime of the facility. Moreover, the timeline for the facility from cradle to grave is needed. (4) *Effluents:* These are the aerial and liquid emissions from the processing step after abatement. (5) *Products:* These include the processed graphite stream, but may also include other items generated as a result of processing the graphite such as spent filters. Requirements for transport need to be determined.

Fig. 7 shows an example of a waste management option for which inputs and outputs at each process stage were defined and data were obtained to enable subsequent evaluation of the option.

5. Conclusion

Over 250,000 tons of i-graphite have been accumulated worldwide, ranging from countries with a fleet of several graphite-moderated power reactors to prototypes, production, and single experimental reactors. The i-graphite is a complex type of waste due to its specific characteristics relating to its irradiation history when used in a nuclear reactor. Owing to its heterogeneous nature and presence of long-lived radionuclide species, i-graphite requires special consideration in terms of its long-term management. This presents specific challenges for the characterization, retrieval, treatment, and disposal of i-graphite.

An integrated waste management approach that is applicable to different countries, sites, and i-graphite wastes has been developed within the European Commission project CARBOWASTE. The approach used a route map for i-graphite to provide the framework for developing a set of waste management options that can be evaluated against economic, safety, environmental, and sociopolitical factors. The developed approach has benefitted from collaboration between a range of organizations and stakeholders, with sharing of knowledge and experience. Significant understanding of potential treatment technologies has been gained through the CARBOWASTE project. The generic approach is also applicable to other radioactive waste management applications.

As part of the approach for the evaluation and comparison of waste management strategies for i-graphite, 24 waste management options have been identified, encompassing the lifecycle stages of retrieval/segregation, treatment, recycle/reuse, and disposal. The purpose was not to dictate a national waste management strategy in relation to i-graphite, but to develop a "toolbox" of techniques that can be screened and evaluated to determine preferred options, dependent upon specific national strategies, constraints, and regulations.

The options are sufficiently comprehensive to span the range of management strategies applicable to different European countries and account for the specific physical, chemical, and radiological characteristics and behavior of i-graphite. It has been important to include both mature and more novel technologies and approaches to ensure flexibility.

It is important to determine the ultimate disposal route at the outset of the evaluation process, as this defines the requirements for the upstream stages, i.e., the type of treatment, waste conditioning, and packaging required. A flowsheet system was found to be a useful tool to allow the tracking of inputs and outputs at each stage of a waste management option, and to provide links to data used in the evaluation of the options.

This approach provides a framework for examining any combination of processes, not just the 24 described in this paper, and that new processes and process properties can be easily added or revised. The toolbox provided a convenient means of comparing processes for the i-graphite system and is applicable to wastes.

Conflicts of interest

There is no conflict of interest.

Acknowledgments

The authors would like to acknowledge the financial support of the European Commission (European Atomic Energy Community—EURATOM) for funding project 211333 in the Seventh Framework Programme for nuclear research and training, and their fellow partners in this research consortium. National Nuclear Laboratory acknowledges cofunding received from the Nuclear Decommissioning Authority Radioactive Waste

Management Directorate, now Radioactive Waste Management Limited (www.nda.gov.uk/rwm, a wholly-owned subsidiary of the Nuclear Decommissioning Authority). The authors would also like to acknowledge the financial support of the NNL "Waste Management Decommissioning and Disposal" Signature Research Programme.

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