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Integrated Waste Management Approach WP 1 Review Report – Nuclear Graphite Overview

Executive summary

The objective of this chapter is to provide the reader with an overall appreciation of the issues associated with irradiated graphite which may need to be considered in the context of decommissioning, treatment and storage.

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
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Chapter Contents

1 Introduction

This chapter provides general background to the manufacture of nuclear grade graphite, its properties and the way in which these properties may change when the material is exposed to a nuclear reactor environment. The objective of this chapter is to provide the reader with an overall appreciation of the issues associated with irradiated graphite which may need to be considered in the context of decommissioning, treatment and storage. Where appropriate, UK Magnox reactor experience will be used to illustrate the behaviour and properties of nuclear graphite. Many of these issues have been elegantly reviewed previously[1,2] and reference should be made to these documents and the references therein for further information on the subject.

2 Production of nuclear grade graphite

A number of processes exist for the preparation of polycrystalline carbons and graphites with a wide range of crystalline perfections and properties. Nuclear grade graphite has been manufactured from cokes produced as a by-product of the petroleum industry, from natural pitch sources and also from naturally occurring graphite (for example, Gilsonite) and the process has been described in a number of texts; one of the more informative accounts is provided by Kelly[3]. A flow chart showing the principal steps in the manufacturing process is provided in Figure 1. The choice of coke, binder and impregnation materials, together with the forming and final heat treatment processes can produce a wide range of properties and will affect behaviour under irradiation.

The process for the manufacture of nuclear graphite involves

- Sourcing of raw materials
- Calcination
- Forming
- Baking
- Pitch impregnation
- Graphitisation
- Purification
- Graphite testing

The primary raw materials for the production of nuclear graphite are calcined coke, coal tar binder and impregnation pitches, softening agents, wetting agents and lubricating oils. Petroleum coke is a by-product of a refining (or coking) process in which heavy residual oil is thermally converted and upgraded into lighter products. In the case of Pile Grade A (PGA) graphite used in the Magnox reactor cores, petroleum coke from the Shell refinery at Pernis in Holland was chosen. The binder pitch for PGA was originally sourced from the Ford Motor Company at Dagenham and refined by North Thames Gas at Beckton in London.
The raw petroleum or pitch coke is first calcined in the temperature range 900-1300°C to reduce the volatile content and prevent excessive shrinkage during later heat treatments. During this process, an essentially disperse system composed of minute crystallites embedded in a matrix of highly condensed aromatic compounds grows into larger crystallites.

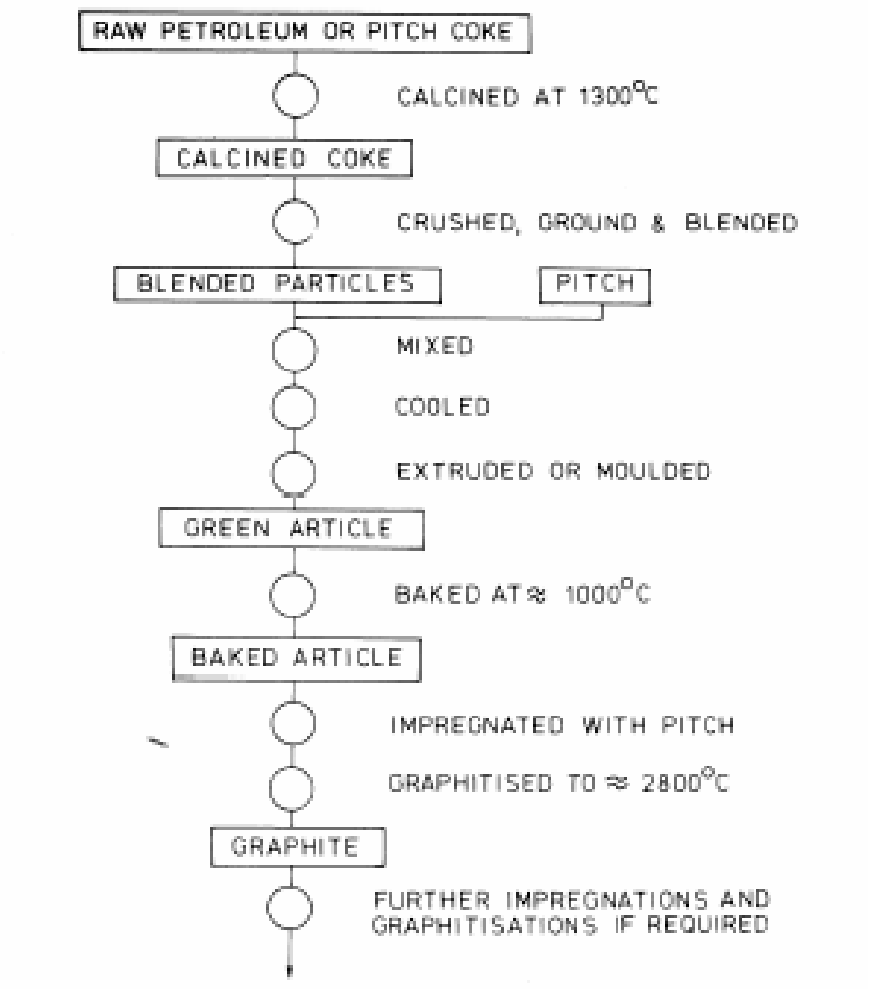

Figure 1 Materials and processes used in the manufacture of graphite (taken from Kelly3)

Following the calcination process, the coke is crushed and milled and then sized into various fractions. Graphite producers have standard mix (or forming) formulations for each size and grade of graphite, these formulations comprising differing proportions of standard particles and 'flour'. The fine particle 'flour' fraction has dimensions of less than about 0.4 mm. The coarse particle fraction may exceed 10 mm depending upon the size and desired properties of the final artefact. In addition to the coke particles, the formulation includes a defined range of binder pitch together with additives to aid forming. The blend of coke and pitch binder produces a plastic mix which is heated to ensure homogeneity of mixing and formed into shape either by extrusion or moulding. Cokes from different sources give powders with various crystallite morphologies and sizes. The properties of the final graphite matrix are strongly dependent upon the source of the coke.

The formed body is baked to coke the pitch binder at temperatures in the range 750-900°C. This process is generally carried out with the artefacts packed in coke, which allows expansion during heating and provides mechanical support. The poor thermal conductivity of the coke and artefacts necessitates a baking cycle taking 30-70 days ensure that all the material has been heated to the desired temperature. This volatilises a part of the pitch binder with the bulk material then showing a loss in density and an increase in permeability.

Depending upon the grade of graphite required, the density and strength can be increased by impregnation with coal pitch tar. The pitches chosen for this purpose must be extremely fluid at the desired impregnation temperature. The material is then re-baked to pyrolise the impregnate pitch in the pores. The number of pitch impregations can range between two and six.

The final graphitisation of the material is carried out in conventional (Acheson) graphitising furnaces at temperatures in the range 2600-3000°C. The material is stacked in a conducting coke bed buried under insulating material. A large electric current is passed through the bed.

The heating cycle generally lasts about 15 days after which the graphite produced is unpacked from the surrounding coke bed.

Purification of nuclear grade graphites is important for minimising neutron absorption. Particularly important in this respect is boron, which has a very large neutron capture cross-section for the reaction B-10 (n, α) Li-7. The problem can be overcome by either selecting very pure coke sources (for example that used for PGA graphite) or by including a purification stage in the production process. Halogens (chlorine gas or freons) have been used to purify graphite for nuclear use. Stable boron carbides that are formed at high temperatures are converted to volatile halides and can be flushed from the graphite. The history of nuclear graphite production in the US for the Hanford production reactors including the evolving requirements for improved purity has been described by Eatherly[4]. The purification process can lead to some undesirable side effects, as the final graphite product may contain some residual amounts of either molecular chlorine or CFC and possibly residual BCl_3. On irradiation, the production of Cl-36 with its extremely long half-life can have implications for decommissioning and disposal.

The graphitisation furnace load or purification furnace load, if applicable, is referred to as a heat. A furnace loading diagram gives the positions of each piece which can be used to identify material for testing. It is normal for all artefacts to be assigned a unique identifier at the forming stage which is retained throughout the manufacturing process. Heat certificate data (representing a heat rather than individual blocks) typically cover ash content, specific heat, ultimate tensile strength, ultimate compressive strength, shear strength, Young's modulus, thermal conductivity, coefficient of thermal expansion and electrical resistivity. Sampling frequencies for historical material vary and records have not always survived. Some typical properties are presented in Section 3.

3 As-manufactured nuclear grade graphite properties

The theoretical density of crystal graphite is 2.266 g cm^{-3}. Polycrystalline graphite has a lower density due to the presence of internal porosity arising during the manufacturing process. The density of the graphite and the nature of the associated porosity will be determined by the type and size of coke used, the manufacturing route and the number of impregnations. Of particular

importance in understanding the behaviour of irradiated graphite is the formation of so-called Mrozowski cracks. These fine cracks are formed during cooling from the graphitisation temperature by the anisotropic thermal contraction of crystallites and can account for between 3-8% of the total porosity. Non-irradiated nuclear graphites have initial densities typically in the range 1.6-1.8 g cm^{-3}.

An ASTM specification now exists for nuclear graphites[5] covering both chemical and physical and mechanical properties. This specification covers isotropic and near-isotropic graphites (isotropy ratio of 1.10-1.15 based on the coefficient of thermal expansion) which would exclude many historical nuclear grade graphites.

The graphite used for the construction of UK Magnox reactor cores was Pile Grade A (PGA) graphite. The coke used for the production of the graphite was referred to as 'needle' coke because of the needle like appearance of the grains after crushing with the needle axis aligning with the basal plane. The method of forming the basic shape of the graphite blocks involved extrusion. This method had the effect of preferentially aligning the needles and hence the crystallite basal planes in a direction parallel to the direction of extrusion. As a result, the properties of the graphite are anisotropic (or more specifically orthotropic, where properties perpendicular to the extrusion direction are isotropic and differ from those in the extrusion direction).

A second grade of graphite using a different coke source was put through the same manufacturing process as PGA, but omitting the final impregnation, to produce Pile Grade B (PGB) graphite. This material was used in the Windscale Piles and early Magnox reactors, and for the side-reflector in later Magnox reactors. Typical properties for these two materials together with those for an earlier grade (AGXP) are summarised in Table 1. This information has been compiled from heat certificate data and from characterisation studies after the cores were built. Typical impurity levels for PGA and PGB graphite are summarised in Table 2.

4 Effect of irradiation on graphite

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 fas neutron irradiation leading to physical, mechanical and thermal property changes
- chemical changes produced by the irradiation chemistry leading to physical, mechanical and thermal property changes
- activation of impurities and transported materials deposited in the graphite pores leading to induced radioactivity

Table 1 Properties of un-irradiated graphite used in UK Magnox reactors

Property	Direction*	Graphite type		
		AGXP	Pile Grade A (PGA)	Pile Grade B (PGB)
Ash content %/w		Not known	0.5 max for binder	Not known
Graphite reactivity to air (µg/g/h at 400°C)		Not known	3.2	Not known
Density (g cm^{-3})		1.64	1.74	1.64
Open pore volume (cm^3/cm^3)		Not known but expected to be similar to PGB	0.2	Not known
Thermal conductivity (W/m/K at 20°C)	Wg/ag	Not known but expected to be similar to PGB	200/109	167/126
Compressive strength (MPa)	Wg/ag	Not known but expected to be similar to PGB	31.0/29.7	Some evidence for the compressive strength being 70% of the value obtained for PGA graphite.
Tensile strength (MPa)	Wg/ag	Not known but expected to be similar to PGB	9.6/7.6	8.3/4.8
Flexural strength (MPa)	Wg/ag	Not known but expected to be similar to PGB	12.0/7.5	Not known
Tensile strain to failure (%)	Wg/ag	Not known but expected to be similar to PGB	0.11/0.22	Not known
Dynamic Young's modulus (GPa)	Wg/ag	Not known but expected to be similar to PGB	9.8/5.4	9.0/4.5
Static Young's modulus (GPa)	Wg/ag	Not known but expected to be similar to PGB	8.2/4.5	Not known
Coefficient of thermal expansion (x 10^{-6} over 20-120°C)	Wg/ag	Not known but expected to be similar to PGB	1.0/2.9	1.5/2.8
Gas diffusivity (diffusion coefficient)		Not known but expected to be similar to PGB	Highly variable but in the region 0.003-0.020	Not known
Gas permeability		Not known but	Not well	Not known

(viscous/Knudsen permeability coefficients)		expected to be similar to PGB	characterised but in the region 1.2 x 10^{-10} /1.3 x 10^{-6}	

* wg = with grain (parallel) ; ag = against grain (perpendicular)

4.1 Irradiation damage

When a fast neutron collides with a carbon nucleus, while passing through a nuclear graphite, atoms are knocked out of their lattice positions and interjected into the immediate surroundings. In this way, one displacement per atom is achieved after a fast neutron dose of approximately 7×10^{20} neutrons cm^{-2} (DIDO Nickel Equivalent). 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 left behind. 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[6]. 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. This issue, which may affect treatment options, is discussed further in Section 5.2 below.

4.2 Radiation chemistry effects

If the graphite is exposed to an oxidising environment (i.e. air or carbon dioxide), the rate of oxidation of the graphite is greatly increased by ionising radiation. This has significant implications for gas-cooled reactors operating with carbon dioxide based coolants. In helium cooled reactors, impurity levels in the gas will determine the extent of oxidation rather than any effect on rate by ionising radiation.

Exposure of graphite to carbon dioxide in the presence of gamma radiation results in radiolytic graphite oxidation. Radiolytic oxidation is initiated by ionising radiation energy - both neutron and gamma - dissipated in the CO_2 coolant. Although appearing to be thermally stable (in fact CO_2 in the presence of carbon is thermodynamically unstable but the thermal rate of reaction is very low) at the molecular level the CO_2 is broken down to CO together with a range of oxidising ions and free radicals. These rapidly recombine to reform CO_2, unless the free radicals impinge first on a graphite surface, in which case they can gasify carbon atoms as CO. In the absence of inhibitors, radiolytic oxidation occurs equally as fast in graphite pores as it does on external surfaces. Moreover, because it enlarges pores, which then contain more gas and accessible surface, there is the potential for the oxidation rate to increase with time. Increases in porosity due to radiolytic oxidation result in a decrease in strength, elastic modulus and thermal conductivity and an increase in thermal resitistivity. These property changes may affect dismantling and treatment options.

A second radiation chemistry effect specific to carbon dioxide cooled reactors is the production of reactive forms of carbon from minor components of the coolant gas, principally through the polymerisation of carbon monoxide. They are deposited within the graphite pores near the surface of components although some are found throughout pore structures. The significance of these deposits is their chemical reactivity in air (which is up to 10^3 times greater than that of graphite). The presence of carbon deposits may influence ways in which waste graphite is

treated due to the exothermicity of the reaction with air and the potential release of containing radionuclides.

4.3 Activation of impurities and transported materials

Activation of impurities (see for example

Table 2) and of transported materials from elsewhere in the reactor (for example, corrosion products) deposited in the graphite is largely brought about through interactions with slow neutrons. This process is unavoidable where suitable parent isotopes are present.

Although graphite used in nuclear plant is extremely pure, nevertheless residual impurities undergo neutron activation, producing radioisotopes including Co-60, Fe-55, C-14, H-3, S-35 and Cl-36.

The major C-14 producing neutron activation reactions in a nuclear reactor are:

- The N-14 (n, p) C-14 reaction with a high thermal neutron capture cross section
- The O-17 (n, α) C-14 reaction with a high thermal neutron capture cross section
- The C-13 (n, γ) C-14 reaction with a low thermal neutron capture cross section.

All of the above reactions can contribute to the C-14 component of irradiated graphite. A large fraction of the C-14 in the CO_2 coolant (of a carbon dioxide cooled reactor) is due to the N-14 reaction. Whilst nitrogen impurities arise during the graphite manufacturing process, impurities in the coolant gas can make a significant contribution. O-17 will originate from the CO_2 coolant.

C-14 is the dominant contributor to graphite activity once short-lived isotopes have decayed (>50 years post closure). The distribution of this isotope approximately follows the thermal neutron flux. Within a graphite block, the isotope is more likely to be present near the surface as most originates from the coolant. C-14 is retained in the graphite and associated carbon deposits primarily as elemental carbon, on surfaces, some oxygen will be associated with it. C-14 produced in reactions other than from C-13 (i.e. from N-14 or O-17) is likely only to be present in surface oxide and in carbonaceous deposits (C/H/O compounds of high molecular weight), which are potentially more mobile in a turbulent flow, but the total activity in this form will be relatively small when safe storage commences.

The sources of tritium are lithium impurity in the graphite, and the fission process in the fuel followed by diffusion through the fuel cladding and absorption by graphite from the coolant. Tritium is transferred from the graphite surface to the coolant with extreme ease[7 8]. This implies that tritiated species on the graphite surface will have exchanged tritium with atmospheric moisture and that this tritium will have been lost very quickly after reactor operation ceased - probably within a matter of weeks. Further releases will depend on the rate of diffusion of tritium within the graphite, which is very much slower than the surface exchange rate but remains significant at reactor operating temperatures.

As discussed in Section 2, halogens (chlorine gas or freons) and halide salts used to purify graphite for nuclear use are the source of Cl-36. If halide salts are used as the source of the graphite purifying reagent (chloride or fluoride salts) then these will first melt and then vaporise (e.g. the boiling point of lithium, sodium, and potassium chlorides all lie in the range 1380 - 1440°C,[9] and give off molecular metal halides, more accurately described as ion-pairs.

These may react with the boron present as impurity in the graphite to give the BCl_3 molecule. All the chlorine bearing species (metal chlorides, chlorine molecules, BCl_3, CFCs) are gaseous at the production temperature but on cooling the metal chlorides (if any persist) would first liquefy and then solidify. These gaseous species can also become physically adsorbed on to the graphite surface. On irradiation in the reactor core the chlorine becomes activated by a neutron capture process, Cl-35 + n → Cl-36. Note that Cl-35 represents about 75% of the naturally occurring chlorine. The remainder (^{37}Cl) undergoes a similar process but is of no consequence as the product Cl-38, has a half-life of about 30 minutes. Decay of Cl-36 is by beta emission with a half-life of 3.1×10^5 years, the daughter product of Cl-36 is Ar-36, one of the stable isotopes of argon. Any chlorine remaining within the graphite or on its surface may be assumed to be strongly bound, otherwise the high temperature and constant gas purge over the surface would remove the chlorine to the reactor coolant gas stream.

Isotopes with relatively short half-lives build up to a steady state level during reactor operation and can be expected to decay relatively quickly after end of generation (for example, Co-60

with a half-life of 5.3 years and H-3 with a half-life of 12.3 years). Such isotopes present a short-term hazard for decommissioning and their presence is a major argument to support a period of 'safe storage' in the reactor before dismantling activities commence. Other isotopes such as C-14 and Cl-36 have long half-lives (5,760 years and 308,000 years respectively) and their presence and mobility require consideration when choosing dismantling, treatment and storage options (noting that a long half life usually implies a low specific activity).

Table 2 Graphite impurity inventory for Magnox reactor graphites based upon heat certificate data

Element	PGA	PGB
Li	0.36	0.14
Be	<0.05	<0.06
B	0.016	0.075
N	10	10
Na	<1.0	4.0
Mg	3.0	10
Al	7.0	60
Si	80	100
S	<50	90
Cl	<2.0	2.0
Ca	80	100
Ti	8.0	20.0
V	40	50
Cr	2.5	1.0
Mn	0.2	0.3
Fe	25	15
Co	<0.03	<0.06
Ni	6.0	6.0
Zn	<0.4	<0.5
Sr	1.0	3.0
Mo	0.4	0.5
Ag	<0.05	<0.6
Cd	<0.03	<0.03
In	0.05	0.06
Sn	<0.15	<0.2
Ba	10.0	30
Sm	<0.04	0.04
Eu	0.008	0.018
Gd	0.008	0.025
Dy	0.015	0.029
W	<0.04	<0.4
Pb	3.0	6.0
Bi	<0.5	<0.3

Impurity concentrations in weight parts per million (wppm)

5 Irradiated nuclear grade graphite properties

As discussed in Section 4, significant changes in graphite properties can arise from exposure to irradiation and to an oxidising environment. By way of illustration, Table 3 provides an overview of the behaviour of graphite used in UK Magnox nuclear reactors. Graphite properties whose changes may be of particular interest in decommissioning and graphite waste management are:

- Mechanical properties (strength, Young's modulus, fracture toughness);
- Thermal properties – thermal conductivity and stored energy;
- Dimensional change;
- Oxidation characteristics;
- Radioactivity.

5.1 Mechanical properties

Graphite is stronger in compression than bending and stronger in bending than in tension. Fast neutron irradiation causes a rapid increase in strength due to pinning of dislocations in the basal planes. Following this initial hardening, there is a further increase in strength with increasing fluence due to structural effects (closure of Mrozowski cracks), until a peak is reached after which the strength decreases due to the generation of new porosity. These strength changes are accompanied by a similar but larger changes in dynamic Young's modulus (and other elastic moduli). If the graphite is also undergoing radiolytic oxidation, then the generation of porosity and the decrease in connectivity within the microstructure leads to a decrease in strength (and modulus). The decrease in strength (and modulus) very approximately follows an exponential decay up to weight losses of about 30%. In PGA graphite, where there is simultaneous irradiation hardening and radiolytic oxidation, the two processes very approximately cancel out at weight losses of ~10-15%, beyond which the decrease in strength due to oxidation dominates. Handling of graphite during disassembly may be affected by changes in fracture toughness. Graphite is a brittle material an dit may become more brittle when oxidised.

Mechanical property variations within graphite components and within graphite structures in nuclear plant can be complex and must be assessed against appropriate flux, temperature and oxidation (for CO_2-cooled plant) histories.

5.2 Thermal properties

Quite small levels of fast neutron damage lead to significant decreases in the thermal conductivity of graphite. With increasing irradiation fluence, thermal conductivity remains at a low value until a threshold, beyond which the structure of the graphite starts to degenerate through the generation of porosity bringing about a further significant decrease in thermal conductivity. Values as low as 2 or 3 W/m/K compared with the non-irradiated values of around 100-200W/m/K can be achieved in graphite irradiated at low temperatures. As with mechanical properties, radiolytic oxidation causes a simultaneous exponential decay (very approximately) in thermal conductivity. The changed heat transfer properties of irradiated graphite must be taken into consideration if, for example, a deep geological disposal route is being considered.

As discussed above, Wigner energy (or stored energy) accumulates in graphite under fast neutron irradiation as a result of atoms being displaced from their normal lattice positions into configurations of higher potential energy. Furthermore, this energy can be released if the graphite is heated above its irradiation temperature. This phenomenon was particularly important for the UK Windscale Piles where the graphite was irradiated at low temperatures (between ambient and 130°C). Under these conditions, a temperature increase could release stored energy at a sufficient rate that the specific heat capacity of the graphite would be exceeded resulting in potential adiabatic self-heating. In 1953, an unexpected rise in the temperature of Windscale Pile 1 during a shutdown was shown to be due to the spontaneous release of stored energy in the graphite moderator[10]. It was later shown that a similar release had occurred on Windscale Pile 2 a few months previously, but that the spread of the release had been checked by force cooling. Frequent monitoring of the low temperature component of the stored energy of the Windscale piles was subsequently carried out[11]. The deliberate attempt to anneal out some Wigner energy accumulated in Windscale Pile 1 was an initiating event in the fire of 1957[12]. As a result of these events, measurements of the rate of release of stored energy on samples taken from UK Magnox reactor cores have become a mandatory component of ongoing graphite core monitoring programmes (even though these reactors have operated at temperatures in excess of the Windscale piles) demonstrating that stored energy is less but not negligible.

Table 3 Properties of irradiated graphite used in UK Magnox reactors

Properties	Direct-ion*	Graphite type		
		AGXP	Pile Grade A (PGA)	Pile Grade B (PGB)
Graphite reactivity to air (µg/g/hr at 400^0C)		Not known	Depends upon location of component in core and operating history. High likelihood of enhancement of unirradiated value.	Not known
Density (g/cm^3)		1.64	Depends upon location in core and irradiation history. Could be in the range 0.9-1.74.	Low flux locations in core so relatively unaffected.
Open pore volume (cm^3/cm^3)		Not known but expected to be similar to PGB.	Depends upon location in core and irradiation history. Could be in the range 0.2-0.7.	Low flux locations in core so relatively unaffected.
Thermal conductivity (W/m/K at 20^0C)	wg/ag	Not known but expected to be similar to PGB.	Affected by fast neutron fluence, temperature and radiolytic weight loss. At $50x10^{20}$ n/cm^2 (EDND), 350C (EDT) and 40% weight loss, 46/25.	Low flux locations in core so relatively unaffected.
Compressive strength (MPa)	wg/ag	Not known but expected to be similar to PGB.	Affected by fast neutron fluence, temperature and radiolytic weight loss. At $50x10^{20}$ n/cm^2 (EDND), 350C (EDT) and 40% weight loss, 5.7/5.7.	Low flux locations in core so relatively unaffected.
Tensile strength (MPa)	wg/ag	Not known but expected to be similar to PGB.	Affected by fast neutron fluence, temperature and radiolytic weight loss. At $50x10^{20}$ n/cm^2 (EDND), 350C (EDT) and 40% weight loss, 1.8/1.5.	Low flux locations in core so relatively unaffected.
Flexural strength (MPa)	wg/ag	Not known but expected to be similar to PGB.	Affected by fast neutron fluence, temperature and radiolytic weight loss. At $50x10^{20}$ n/cm^2 (EDND), 350C (EDT) and 40% weight loss, 2.2/1.4.	Low flux locations in core so relatively unaffected.
Tensile strain to failure (%)	wg/ag	Not known but expected to be similar to PGB.	0.11/0.22	Not known
Dynamic Young's modulus (GPa)	wg/ag	Not known but expected to be similar to PGB.	Affected by fast neutron fluence, temperature and radiolytic weight loss. At $50x10^{20}$ n/cm^2 (EDND), 350C (EDT) and 40% weight loss, 3.1/1.9.	Low flux locations in core so relatively unaffected.
Static Young's modulus (GPa)	wg/ag	Not known but expected to be similar to PGB.	Affected by fast neutron fluence, temperature and radiolytic weight loss. At $50x10^{20}$ n/cm^2 (EDND), 350C (EDT) and 40% weight loss, 2.9/1.7.	Low flux locations in core so relatively unaffected.
Coefficient of thermal expansion (x 10^{-6} over 20-120^0C)	wg/ag	Not known but expected to be similar to PGB.	Affected by fast neutron fluence, temperature and radiolytic weight loss. At $50x10^{20}$ n/cm^2 (EDND), 350C (EDT) and 40% weight loss, 1.5/4.9.	Low flux locations in core so relatively unaffected.
Gas diffusivity (diffusion coefficient)		Not known but expected to be similar to PGB.	Increased by radiolytic weight loss. At 20% weight loss, estimated to be in the range 0.020-0.080.	Low flux locations in core so relatively unaffected.
Gas permeability (viscous/Knudsen permeability coefficients)		Not known but expected to be similar to PGB.	Increased by radiolytic weight loss - highly variable and poorly characterised.	Low flux locations in core so relatively unaffected.

The potential risk of triggering an inadvertant release of Wigner energy while handing and processinsg individual graphite blocks during decommissioning is small but requires assessment. The potential for releasing Wigner energy during any storage period, during packaging and treatment processes and under final waste repository conditions is small but would also require assessment.

The influence of impurities/contaminants on stored energy has received some attention, but in comparison to the bulk of the Wigner energy studies such work has been somewhat limited. Studies with contaminants have had no measurable effect but it was found that boron has the potential to affect the accumulation of stored energy. Increasing the concentration of boron produces an increase in the amount of stored energy and lowers the threshold annealing temperature. This may be an issue for reactors that employed boronated graphite, such as the UK Dounreay Fast Reactor.

5.3 Dimensional change

As discussed above, fast neutron irradiation of graphite leads to dimensional change in crystallites and to a lesser extent in polycrystalline material. In the presence of a flux gradient, graphite components will undergo dimensional change rates will differ leading to the development of strains and hence distortion. The distortion of graphite components could lead to problems in the disassembly of core structures.

5.4 Oxidation characteristics

Two issues relating to oxidation need consideration.

- Oxidation will affect the thermal and mechanical properties of the graphite, as discussed in Sections 4.1 and 4.2, and therefore potentially the integrity and handling of components.
- The oxidation characteristics of the graphite may change over the period of reactor operation, potentially affecting treatment and disposal options.

If the graphite has undergone oxidation over the operating period of the nuclear reactor then, as discussed above, then some assessment of its effect upon mechanical properties must be undertaken in order to address decommissioning options. In the case of UK Magnox and AGR reactors, radiolytic graphite oxidation has been monitored extensively and oxidation models

have been successfuly developed to predict future behaviour. In the case of the UK Windscale Pile 1 that suffered a fire in 1957, the extent of thermal oxidation of the core may be less well characterised. In terms of graphite component integrity and component mechanical properties, nuclear plant must be assessed on a case by case basis, based upon operating history and oxidation models where appropriate.

Post-irradiation oxidation characteristics (air reactivity) of the graphite must be taken into account when assessing treatment and disposal options. If the graphite operational environment was carbon dioxide, then radiolytic oxidation will have increased the porosity and hence the chemical oxidation rate in air. In addition, the formation of more reactive (compared with the substrate graphite) carbonaceous deposits on the surface of components and within the pores will also increase chemical oxidation rates in air. There is also evidence for radiation enhancement of oxidation rates by activation of reacting surfaces by neutron fluence.
There are many literature references relating to the graphite-air reaction and these have been extensively reviewed recently[1,2,13]. The catalytic activity of specific inorganic impurities is also well researched, for example[14,15]. This has enabled the propensity for catalysis of impurities either initially present in small quantities, or potentially entrained into the reactor vessel through in-leakage of rainwater during storage to be quantified.

The routine monitoring programmes during operation of the UK Magnox reactors has regularly confirmed the very modest rates of reaction for graphite in air (typically less than 100µg g^{-1} h^{-1} at a standard temperature of 450°C) and also verified the activation energy for the oxidation reaction (typically around 35-40 kcal mol^{-1} or 145-170 kJ mol^{-1}). The quantities of carbonaceous deposit associated with the graphite moderators of the AGRs and most Magnox reactors are sufficiently small that their properties are not of major concern under normal circumstances. If, however, an incineration process is eventually chosen as the graphite disposal route, when such deposits will oxidise much more readily than graphite itself, then further consideration would be needed. This would equally apply to any operation giving rise to significant temperatures.

5.5 Radioactivity

As discussed in Section 4.3, graphite will become radioactive via a variety of mechanisms. This radioactivity needs considering when choosing treatment and disposal options.

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